EVALUATION OF CURRENT AND PROPOSED ANALYTICAL TECHNIQUES FOR

TRACE ELEMENTS IN AGRICULTURAL DRAINAGE EVAPORATION PONDS

OF THE SAN JOAQUIN VALLEY OF CALIFORNIA

March 27, 1990

Final Report

to:

California Regional Water Quality Control Board
Central Valley Region
3443 Routier Road
Sacramento, CA 95827-3098

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DISCLOSURE STATEMENT

This final report was prepared through agreement 7-128-150-2
the amount of $66,303 with the State of California Water
Resources Control Board (SWRCB). The contents of this document
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I. FOREWORD

Evaporation basins are being used extensively in the San Joaquin Valley, California, for disposal of agricultural subsurface drainage waters. Approximately 3,000 hectares of evaporation basins are in current use with an additional 20,000 hectares planned. As their use expands, concerns are being raised regarding increasing trace element concentrations that could pose environmental hazards similar to those associated with selenium at Kesterson Reservoir and National Wildlife Refuge (Westcot et al., 1988, 1989).

Federal and state laws define concentration limits for many trace elements in waters because they are known to produce toxicity effects in animals and/or plants when present at low concentrations. Control agencies must therefore be assured of the accuracy and reliability of trace element measurements in waters to achieve fair enforcement policies.

Trace element analyses in nonsaline waters is relatively simple, reliable and accurate compared to measurements in highly saline waters. Detection limits for trace elements in saline waters are often unusually high. This is due to several factors including the higher viscosity of saline waters and to matrix effects which are unique with each laboratory method and instrumentation. Rasmussen (1981) and Sturgeon et al. (1980) discussed analytical problems associated with trace element analyses in sea water. Since the salt content of pond

waters is often higher than sea water and has a high sulfate to chloride ratio (Westcot et al., 1988), analytical problems are amplified.

This project was undertaken to resolve as many of the problems associated with sampling, storage and analyses of trace elements in saline waters as possible within the time, financial, instrumentation, and other constraints associated with the effort.

The results reported herein are organized under subheadings of the table of contents.

II. SUMMARY

The objectives of this project were to address the problems associated with sampling, storage and reliable analyses of trace elements in highly saline evaporation pond waters of the San Joaquin Valley. Since these waters were known to contain relatively high concentrations of several trace elements, priority was given to developing and testing simultaneous multielement analytical methods and instrumentation which would be relatively fast, reliable and cost-effective.

The project report includes a review of the literature relative to problems and recommendations associated with sampling, storage and analyses for trace elements in waters, and in particular, highly saline waters. Information is included on the pros and cons of acidification, filtration, container type and storage time in preserving sample

integrity suitable for subsequent chelation and solvent extraction of multiple trace elements, and final analyses using simultaneous multielement inductively coupled argon plasma-optical emission spectroscopy instrumentation.

Of the many chelation and/or solvent extraction methods reported in the literature for separation and preconcentration of one or several trace elements from saline and other interfering background matrices, features of several methods were selected as most promising and combined in a final method. This was extensively tested for efficiency of recovery of spiked trace elements from a purified, naturally saline background solution (Salton Sea water). Testing of this method represented the major effort of the project.

Preconcentration of 23 trace elements from saline waters buffered with ammonium acetate to pH 5.0 was found effective using multi-element chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction into chloroform. Recovery percentages of elements at low $\mu g\ L^{-1}$ levels in spiked saline Salton Sea water ranged from 90-100%. Uranium in pond water samples determined by the extraction method and molybdenum determined directly in a 1+9 sample dilution compared favorably with results from independent laboratories using different methods. Samples contained a wide concentration range of uranium and molybdenum in a diverse background matrix of sodium, magnesium, chloride, sulfate, etc.

Collection of pond water samples in acid cleaned polyethylene containers followed by transfer to the laboratory in a cooled, darkened

container, and filtration through a 0.45-µm Millipore filter within 24 hours is recommended for determining soluble constituents. This procedure is supported by literature reports of sample contamination from acidification and a requirement of a near neutral pH control of samples pretreated by the recommended extraction method. Filtration of samples through a 0.45 µm Millipore filter within 24 hours of sampling is recommended for subsequent storage and analysis to prevent loss of trace elements from solution by occlusion with precipitation of suspended material.

Recommendations for future study follow: 1) Determine the significance of adsorption of different soluble trace elements by the container material by spiking filtered pond waters, and solvent extract separate aliquots after different storage intervals. 2) Test ways to minimize or prevent container adsorption of trace metals, especially mercury and silver, without acidification of samples. Rinsing cleaned sample containers with a 1% solution of APDC chelate (see extraction method, Appendix A) just before sample collection might prevent trace element adsorption by the container surface. 3) Investigate matrix matching of samples with standards to improve trace element analyses directly in sample dilutions. 4) Analytical and possibly environmental concerns would be better served if sediment samples were dissolved (see Appendix D) and analyzed rather than water totals, and the results interpreted by comparison with measured components in filtered (0.45 µm) samples defined as soluble.

III. SAMPLING AND STORAGE OF HIGH SALINITY WATER SAMPLES
FOR TRACE ELEMENT ANALYSIS

A. Review of Literature

The following comments from the literature include references to studies with both saline and nonsaline samples since few references were found relative to only saline water, and results may have significance for both matrices.

1. Adsorption to Container

Significant losses of trace elements from sample solutions via absorption onto the walls of sample containers have been verified by several studies. Struempler (1973) studied the adsorption character-istics of silver, lead, cadmium, nickel and zinc onto borosilicate glass, polyethylene and polypropylene container surfaces. He found that nickel was always adsorbed but that zinc and cadmium were not adsorbed by polyethylene. Silver was best stored in darkened polyethylene con-tainers. If samples were acidified to pH 2 with nitric acid, the adsorption of silver, lead, cadmium and zinc onto borosilicate glass was prevented, as was the adsorption of silver onto polyethylene. Robertson observed negligible loss of zinc, caesium, strontium and

antimony from seawater samples over 75 days stored in Pyrex and polyethylene containers provided the samples were acidified to pH 1.5 with dilute hydrochloric acid. Indium, iron, silver, cobalt, rubidium, scandium and uranium underwent losses from samples stored in polyethylene at pH 8 but only scandium and uranium were lost when the samples were acidified to pH 1.5.

Silver and mercury are particularly prone to adsorption losses. West et al. were unable to find a satisfactory method for eliminating silver adsorption from aqueous solutions. Rosain and Wai (1973) observed severe losses of mercury(II) at pH 2, and less adsorption at pH 0.5 in nitric acid. They also observed severe losses of mercury stored in polyvinylchloride containers compared to polyethylene and soft glass. Dokiya et al. (1974) studied losses of mercury and zinc added to marine water samples and found that mercury losses were greater from filtered natural samples than from synthetic seawater samples.

Mullin and Riley (1955) found polyethylene containers to be satisfactory for storage of seawater samples prior to silicate determination provided the water was filtered and stored at pH 2.1-2.5. Unfiltered acidified and non-acidified water samples showed a steady weekly increase in silicate content. Murphy and Riley (1956) found that polyethylene containers were unsuitable for storage of seawater samples for phosphate determination because of strong adsorption of phosphate anions.

Dolinsek and Stupar (1973) noted large losses of lead from lead nitrate solutions, even after 5 minutes storage in borosilicate glass containers: polyethylene adsorbed less. The adsorption was prevented by the addition of hydrogen peroxide or nitric acid. Shendrikar and West (1974) studied the adsorption of Cr^{+3} and Cr^{+6} on selected surfaces. The loss of Cr^{+3} after 15 days was 25% in polyethylene at pH 6.95, but much less at pH 3.1 or in 0.5 M nitric acid. Cr^{+6} losses were <1% up to pH 6.95.

2. Volatilization Losses

Jenne and Avotins (1975) concluded that the most important factor causing the loss of mercury from solution is bacteria and other microorganisms. Even sterilization of the sample plus container does not suffice since the enzyme systems remain active. The capability of many microorganisms to survive strong acidification and freezing may explain the unreliability of these preservation techniques where aliquots are to be taken for analyses.

Coyne and Collins (1972) observed a 90% loss of mercury within one to two hours from polyethylene containers!

Thompson-Eagle et al. (1980) measured selenium volatilization as dimethylselenide from agricultural evaporation ponds. Selenium is one of several hydride forming elements (As, Sb, Bi, Ge, Sn, Te, Pb) which conceivably could also be volatilized by microbial action.

The above studies, although not exhaustive in number, indicate the complexity of the problem in relation to different elements and different container material. The problem is further complicated if one recognizes that container materials probably vary in surface characteristics and contamination as a function of their method of construction and past chemical and physical history (Kuehner et al., 1969). It is difficult to make valid generalizations when conflicting results have been reported by different groups of workers.

Dolinsak and Stupor (1973) observed that the amount of an analyte element adsorbed does not vary significantly over a wide concentration range. As the analyte element concentration decreases, the significance of absorption losses increases rapidly. Whereas at high analyte concentrations the adsorption losses become less significant.

3. Contamination from Container Materials and/or Added Preservatives

Minczewski (1967) rated several container materials in the following order of preference to avoid contamination from material to sample: polyfluorocarbons (Teflon) > polyethylene > vitreous silica > platinum > borosilicate glass. Teflon, however, is not free from impurities. Microscopic examination of Teflon (FEP) bottles has revealed imbedded particles which contain iron, zinc, aluminum, copper and manganese among the constituents which are acid leachable (National Bureau of Standards, 1968). Inclusions undoubtedly originate from the molds during fabrication. Permeation tests with different polymers show

Teflon to be the least permeable, however, permeation rates increase with temperature for all polymers (Kuehner and Freeman, 1969). The microscopic voids that allow permeation are also responsible for adsorption. For example, Teflon beakers containing urine samples are frequently discolored with organic constituents which are not readily removed by extended cleaning. Polyethylene is considerably more permeable to chemicals than Teflon.

Bothner and Robertson (1975) found that mercury contamination could be introduced to sea-water samples stored in polyethylene containers, but could detect no such contamination from borosilicate glass containers.

Ritchie et al. (1972) described compounds of barium, calcium, cadmium, phosphorus, lead and zinc used as stabilizers, of phosphorus and sulfur as antioxidants and ultraviolet absorbers along with fillers of asbestos, glass fiber, talc, clay, barium sulfate, calcium carbonate, calcium fluoride, antimony oxide, titanium dioxide, zirconium dioxide, molybdenum disulfide, aluminum, aluminum oxide, copper and bronze.

Low-density polyethylene is preferable to the high density form because it has a lower content of aluminum, chromium, cobalt, zinc and titanium (Zief and Mitchell, 1976). Polyethylene is probably the most common polymer used in the laboratory and for sample storage because of its low metal content, low price and relative resistance to aqueous solutions of standards and reagents (Zief and Mitchell, 1976).

4. Filtration

Jenne and Luoma (1975) list the following trace element sinks and their respective uptake and release processes in waters.

Sinks	Processes
Oxides (hydrous, amorphic) manganese and iron aluminum and silicon	Surface exchange Diffusion exchange Co-precipitation
Organic substances	Exchange, complexation, chelation
Biota	Passive and active uptake, exchange complexation, chelation
Carbonates, phosphates, sulfides, basic sulfate and chloride salts	Precipitation, co-precipitation, surface (isomorphic) exchange

Florence and Batley (1975) and Hayes et al. (1975) suggest metals in sea water are present either as organic chelates, adsorbed on, or occluded in organic or inorganic particles. Riley and Skinow (1965) recommended filtration through 0.45 μm membrane filters to remove trace metals adsorbed on suspended inorganic and organic detritus in sea water.

5. Shelf Life of Preserved or Non-preserved Samples

Rasmussen (1951) found no significant differences in trace element content between sea water samples preconcentrated directly after sampling on-board ship and samples preserved only by freezing and analyzed in a laboratory several weeks later. Sturgeon et al. (1980)

observed good agreement between different analytical methods for the

measurement of trace elements in sea water which had been filtered

through a 0.45 μm membrane filter acidified to pH 1.6, and stored in

pre-cleaned polypropylene containers for two months.

6. Need for Additional Preservation Techniques to Ensure Reproducibility

The work of Rasmussen (1981) and Sturgeon et al. (1980) with sea

water supports our recommendation that pond water samples be collected

in acid cleaned polyethylene containers, filtered within 24 hours

through 0.45-μm Millipore filters and stored in a darkened cool room

to ensure reproducibility of most soluble trace element analyses.

B. Evaluation of Current Sampling Techniques Used by the RWQCB for
   Analyses of Soluble Trace Elements in Saline Evaporation Pond Waters

Acidification, filtration and cooling of pond water samples

collected in polyethylene containers are discussed below.

Rasmussen's (1981) results showed low, insignificant losses of

trace elements in non-acidified sea water samples stored several weeks

in polyethylene containers. Acidification is a potential source of

contamination of samples from impurities in the acid and/or from acid

dissolution of container materials. Lead contamination from

hydrochloric acid was reported by Rasmussen (1981). Our use of reagent

grade HCl for hydride analyses showed as much as 200 μg L^{-1} mercury

contamination in different lots. Potential chemical transformations associated with acidification may effect subsequent analyses of different elements. For example, we observed approximately a 10% loss per day of selenium in standards prepared in 6 N HCl. This was associated with the appearance of a red suspension in the container, suggesting that soluble selenium was reduced to the metallic form in 6 N HCl. Since near-neutral extraction pH control is necessary for the solvent extraction method (Appendix A), acidified samples would have to be pH-adjusted thus adding another step in the procedure and another source of contamination. Acidifying samples is not recommended.

Visual inspection of agricultural evaporatiuon pond waters reveals a high level of biological activity and suspended material. Although the studies by Rasmussen (1981) and Sturgeon et al. (1980) were not especially designed to study sampling and storage conditions, their work showed that cooling and filtration reduces the potential for losses of trace elements by volatilization and precipitation as discussed by Jeanne (1975). These extensive studies are cited to emphasize the importance of cooling and filtration (0.45 μm) to mini-mize trace element losses during storage. Filtration was evidently not a source of trace element loss or contamination of sea water samples containing sub μg L^{-1} concentrations of trace elements (Sturgeon et al., 1980), and is therefore recommended for evaporation pond water samples. Filtration should be done as soon as possible

after sampling (within 24 hours) to minimize biological and chemical effects on trace element solubility. Additional comments on the importance of filtering samples are found in Section IV.C, and on potential salt precipitation from cooled samples in Section VI.

IV. HIGH SALINITY MATRIX INTERFERENCES IN LOW LEVEL TRACE ELEMENT ANALYSES

A. Review of Existing Analytical Methods

High salinity matrix interferences are considered here for EPA Method 6010 (ICAP-OES) only since this is the only fast, simultaneous multielement instrumentation which is available and meets the time and cost-effective objectives of the project. This instrumentation also permits full utilization of the multielement pre-concentration methods where salt matrix effects are eliminated for the extracted elements. Salt matrix effects are therefore only significant for elements not extracted and present in sample dilutions at concentrations above the instrument detection limit. For most evaporation pond water samples these elements are Si, B, Sr, Li and Mo.

EPA Method 6010 (inductively coupled argon plasma method) identifies the following interferences, all of which may result from a high salt matrix.

1. Spectral interferences:

a. overlap of a spectral line from another element

b. background contribution from continuous or recombination phenomenon

c. unresolved overlap of molecular band spectra

d. background contribution from stray light from the line emission of high concentration elements.

2. Physical interferences:

a. effects associated with sample nebulization and transport processes resulting from change of sample solution viscosity and surface tension caused by a high salt matrix

b. salt buildup on nebulizer tip which affects sample aerosol flow through the torch

3. Chemical interferences:

a. molecular compound formation

b. ionization effects

c. solute vaporization effects

Most of the above interferences can be eliminated by sample dilution. This, however, may result in concentrations of some elements below the instrument detection limit. We analyzed all pond water samples at a 1+9 and a 1+99 dilution and statistically compared the results of 22 randomly selected samples. The results show acceptable comparisons of concentrations of Si, Sr, B and Mo in the two dilutions as indicated

by the following R^2 values: Si, 0.943; Sr, 0.98; B, 0.93; and Mo, 0.935. Regression analysis plots are shown in Appendix C.

This points out that matrix interference effects are not a major concern for these elements in a 1+9 dilution where concentrations are well above the instrument detection limits. Li, Al, P and Ba concentrations were below the detection limit in either and/or both dilutions of most samples, so a similar comparison of the two dilutions was not possible for these elements. Other separation and preconcentration methods would have to be used for low concentration measurements of Si, Sr, B, Li, Al, P and Ba in pond water samples. A dilution of 1+99 or greater is necessary for major element analyses to measure instrument response in a linear concentration range. Further details will be discussed, and detection limits listed in Section F.

B. Organic Interferences

High concentrations of especially low molecular weight and volatile organic compounds either extinguish the plasma or cause instability due to fluctuating gas pressure as the gas passes through the high temperature (8,000 - 10,000°K) of the plasma. More than 30 aliphatic and aromatic liquids were nebulized into a plasma by Miyazaki et al. (1982) who showed that organic solvents with high vapor pressures such as methanol, ethyl acetate, hexane, benzene and cyclohexane were troublesome, whereas solvents with low vapor pressures were not. Five minutes of low temperature (<65°C) pre-heating of samples containing low concentrations

of low molecular weight organics would correct the problem without

loss of volatile sample constituents.

C. Total vs. Dissolved Concentrations of Trace Elements

Concerns raised by the above subject heading should first be put
into perspective by raising the question as to what constitutes a pond
water sample vs. a pond sediment sample. The significance of answers to
these questions can be shown by contrasting the appearance of a sample
collected at the sediment water interface with one collected near the
pond surface. The sample collected near the pond bottom will likely
contain a large visible proportion of solid and suspended material which
will evidently have to be filtered and the separate phases analyzed by
distinctly different methods. The same considerations apply to the
sample collected near the pond surface except that the proportion of
sediment is smaller and therefore the need to separate the phases is
less evident.

Filtration of sea water through a 0.45 μm membrane filter has been
generally accepted as a practical procedure for removing most of the
solid and suspended material (Rasmussen, 1981; Sturgeon et al., 1980;
Riley, 1965; Florence and Battey, 1975).

We separated suspended material from several pond water samples
by filtration through a 0.45 μm Millipore filter and then acid digested
and analyzed the residue. Principal cation components present were in
the order of concentration: Na > Mg > K > Ca with traces of Si, Sr, B,
Al, Fe, Mn, Cu, Zn, V, Mo and Ni. Variable amounts of suspended material

such as algae removed with sample aliquots from unfiltered, stored samples would therefore be a source of error in both soluble and total trace element analyses. Our recent analyses of algae samples from Peck and Lost Hills evaporation ponds showed concentrations up to the following levels (mg kg^{-1} dry weight) for different elements: B 533, Fe 1600, Mn 38, Cu 33, Cd 28, V 27, Mo 384, Ni 15, Cr 85, U 75, and Se 121. Thompson (1986) concluded that algae surfaces are literally a mosaic of metal binding sites and discussed reports that heat-killed algae display a binding capacity for uranium three times greater than living algae. Algae have a high selective affinity for binding uranium (Nakajima et al., 1981).

The above observations and comments in the literature led to the conclusion that filtration of pond water samples is necessary to separate the soluble and solid phases for separate analyses. Samples with a high solids content also cause physical problems during analyses by clogging the nebulizer.

We constructed a simplified plastic container and holder for 0.45 μm membrane filters which allowed rapid vacuum filtration for up to about 50 ml of pond water in less than 5 minutes before the filtration slowed. The same filter membrane was then reverse-flushed with distilled water and the excess water removed by vacuum. The membrane was then restored to its original position for filtering additional aliquots of the same sample. Six 50 ml portions of a 300 ml sample can be filtered in 10 minutes. Filtration is recommended as a laboratory procedure within 24 hours of sample collection.

D. Valence

EPA Method 6010 for inductively coupled argon plasma-optical emission spectroscopy refers to ionization effects under a heading of potential chemical interferences and concludes that this effect is not normally pronounced with ICAP-OES. Fassel and Kniseley (1974) attribute minimum interference effects in the plasma to its high temperature, long residence times in the plasma by sample species and the inert environment provided by the plasma. The ICP tends to minimize matrix and chemical interferences according to Greenberg et al. (1985).

E. Specific Salt Effects

High dissolved solids in samples cause physical effects associated with sample nebulization and transport processes in the nebulizer assembly but are not salt-specific. These effects are caused by changes in viscosity and surface tension which affect the percent of the sample reaching the plasma. The use of a peristaltic pump in the sample delivery system reduces these interferences as does sample dilution. Another potential problem described by EPA Method 6010 is salt buildup from high salt samples on the tip of the nebulizer. Our nebulizer assembly uses a peristaltic pump and the nebulizer tips are constructed from Teflon to reduce the physical effects described above.

Fassel and Kniseley comment that the favorable environmental factors associated with the plasma overcome most interelement or matrix interference effects found in many flame, arc and spark discharges used with other types of analytical instrumentation. They observed up to a

15% depression of a calcium line emission as the sodium concentration was increased from zero to 0.7% in solution.

Preconcentration of trace elements from a high salt matrix solves two analytical problems: 1) High salt matrix effects are eliminated for extracted elements. 2) Concentrations of trace elements near the detection limit in samples are more reliably measured at higher concentrations following extraction.

High recovery percentages of spiked trace element additions to purified natural Salton Sea water shown in Table 2 of the extraction method (see Appendix A), and good recovery of most spiked trace element additions to different "real" pond waters containing a variety and a wide concentration range of major cations (Ca, Mg, Na, K) and anions (Cl^-, $SO_4^=$) (see Appendix C) indicates there is no significant interference from major salts on the efficiency of the trace element extractions from saline water samples. This conclusion is supported by the work of others (Sturgeon et al., 1980; Rasmussen, 1981).

Application of the extraction method has limitations in the case of samples such as acid dissolved sediments and/or water samples containing high concentrations of extractable elements. In dissolved sediment samples, salt matrix effects due to high iron and manganese can be controlled by working with small sample aliquots. No matrix effects due to iron and manganese were encountered in pond water analyses. However, problems were observed with pond waters containing high molybdenum due to emission intensities from molybdenum exceeding a

linear response. In these cases molybdenum levels were lowered by
dilution of the final extracted solution.

A high salt matrix has some adverse effects on both the plasma and
in some cases the extraction method, but the effects are minimized
compared to other instrumental methods, and in both cases can usually
be resolved by sample dilution.

F. Method Detection Limits

The method detection limit (MDL) is defined in EPA Method 6010
(Inductively Coupled Plasma Method) as the minimum concentration of a
substance that can be measured and reported with 99% confidence that the
value is above zero. A table listing estimated instrument detection
limits for a number of elements is included in Method 6010 with the
comments that MDL concentrations were obtained using reagent water,
and similar results were obtained using representative wastewaters.
MDL values actually achieved in a given analysis will vary depending on
instrument sensitivity and matrix effects. The terms MDL and estimated
instrumental detection limits are referred to interchangeably by EPA
Method 6010.

Table 1 in the attached extraction method (Appendix A) lists
estimated instrumental detection limits measured with our instrumenta-
tion using trace element solutions prepared in deionized distilled water.

Concentrations of several trace elements in pond waters are less
than the concentrations listed in Table 1 and are therefore not
measurable even if samples could be introduced directly into the

instrument. Direct introduction of samples is not feasible due to the high salt matrix effects discussed in Section D. Diluted samples can be introduced, but dilution further reduces the concentrations of elements already too low to be measurable in the original sample. An alternative approach is to chemically manipulate a large volume of sample to concentrate trace elements into a small solution volume which is then introduced into the instrument (Chelation and Solvent Extraction of Trace Elements from Saline Waters for Analysis by ICP-OES; see Appendix A). Consider cadmium, for example. The detectable level for cadmium listed in Table 1 is .004 mg L^{-1}. Assume that a pond water sample contains .002 mg L^{-1} Cd which is less than detectable. Suppose 100 ml of this sample is treated by the extraction method and nearly all the cadmium is removed from the salt solution and concentrated in 1 ml which is then analyzed. The concentration of cadmium in the 1 ml of salt-free solution is 0.2 mg L^{-1} (100 x .002 = .2). This concentration is much greater than the detectable limit and can therefore be reliably measured provided contributions of cadmium from reagents (blanks) are known and random sources of contamination minimized. In the above example, the detectable concentrations for cadmium listed in Table 1 has been lowered by a factor of .01 (.01 x .004 = .00004 mg L^{-1}).

Molybdenum is best determined directly in 1:9 dilutions of most pond water samples high in molybdenum. This avoids problems with a nonlinear instrument response from high molybdenum concentrations in solutions of extracted samples. The extraction method (Appendix A) is recommended for samples containing low µg L^{-1} molybdenum concentrations (<100 µg L^{-1}).

Since not all pond water samples can be concentrated by the same factor because of varying concentrations, particularly of molybdenum and uranium which cause matrix effects, concentration factors vary from 10- to 100-fold. Taking into consideration these varying concentration factors, contributions of contaminants from blanks and random contamination, the estimated achievable detection limits for most extractable elements is 0.001 mg L^{-1}. Sturgeon et al. (1980) and Rasmussen (1981) measured trace element concentrations in sea water in the range from approximately 0.005 to 0.0001 mg L^{-1} by preconcentration using chelation solvent extraction and ICAP-OES analyses.

Table I lists the estimated sample detection limits for different elements analyzed in original separate sample aliquots.

TABLE I.

ESTIMATED DETECTION LIMITS IN POND WATER SAMPLES

(mg/L)

In 1+9 Sample Dilutions		By Extraction Method		By Hydride Generation	
Ca	0.5	Fe	0.001	Hg	0.001
Mg	0.2	Mn	0.001	Se	0.001
Na	2.0	Cu	0.001	As	0.001
K	5.0	Zn	0.001	Sb	0.001
P	0.5	Cd	0.001	Bi	0.001
Si	0.10	Pb	0.003	Te	0.001
B	0.05	V	0.001	Ge	0.005
Ba	0.05	Mo	0.001		
Sr	0.10	Ni	0.001		
Li	0.10	Co	0.001		
Ti	0.10	Cr	0.001		
Al	0.30	Tl	0.001		
Be	0.001	Ga	0.001		
Sc	0.010	U	0.010		
Mo	0.08				

V.   DESCRIPTION OF PREFERRED ANALYTICAL METHOD

As a result of extensive testing and experimentation with different approaches to the analyses of evaporation pond waters over the past year, it has become apparent that several different aliquots must be taken from each sample and pretreated by different methods to achieve reliable analytical results for multiple trace elements. It is assumed here that a 300 ml sample has been collected in a screw-cap acid-washed polyethylene container and stored in a cooled, darkened container before and after filtration through a 0.45 μm Millipore filter as described in the following section (Section VI). The recommended sequence and analytical procedures are described below.

1.   Take a 1-ml aliquot from each sample in a set and add 9 ml of deionized-distilled water (DIDW) to make a 1+9 sample dilution. From this prepare a 1+99 dilution. Analyze each set of dilutions as described on page 7 of "Analytical and Quality Assurance Program for Inductively Coupled Argon Plasma Optical EMission Spectroscopy (ICAP-OES) Laboratory" (see Appendix E). See Table I for elements measured in this aliquot.

2.   Take a 50-ml aliquot from each of 4 samples and process through the preconcentration procedure to the analytical step as described in the attached extraction method (see Appendix A). Repeat the preconcentration procedure to the analytical step in sets of 4 samples until about 50 samples have been extracted, and then analyze as a set as described on page 7 of Analytical Program (see Appendix E). See Table I for elements measured in this aliquot.

3. Take a 10-ml aliquot from each of up to 50 samples as a set and add 10 ml of concentrated HCl in a 30-ml borosilicate glass disposable tube (20 x 150 mm). Heat samples in a boiling water bath for 45 min to reduce selenium, cool, adjust volume to 20 ml and analyze by continuous flow hydride generation using ICAP-OES [our procedure is modified from the method of Thompson et al. (1978)]. See Table I for elements measured in this aliquot.

Analytical methods in general have advantages and deficiencies. The above method for analyses of pond waters is no exception. Following are some advantages and deficiencies.

Advantages:

1. Although at least three different aliquots must be pretreated and analyzed separately, the relatively rapid and simultaneous features of the pretreatment and analytical steps are attractive.

2. Many trace elements can be measured and/or looked for at low concentrations in samples.

3. Several elements can be measured and/or looked for separately in each aliquot. This increases confidence in the results where they compare favorably and/or alerts the analyst to problems if the results are divergent.

4. A relatively small original sample volume (approximately 300 ml) provides sufficient sample for approximately six replicate analyses. This conserves time and space required for sampling, filtration and cold storage compared to using much larger sample containers.

<u>Deficiencies:</u>

1. Not all trace elements of interest can be extracted by the chelation solvent extraction method. Recovery tests with silver have shown a wide range in the percent recovered from 20-90%, suggesting that good recovery is possible but as yet we have not been able to identify what causes the variation.

2. Smaller sample aliquots must be re-run through the extraction process if extractable elements are too high and cause matrix interferences.

3. Regression analyses comparing trace element concentrations measured in 1+9 and 1+99 dilutions of 22 samples showed R^2 values of Si, 0.943; Sr, 0.98; B, 0.93 and Mo, 0.935 (see Appendix C), indicating somewhat acceptable measurements within this dilution range. However, these measurements can probably be improved by filtering samples and by calibrating the instrument at salt matrix backgrounds closer to sample levels.

VI. DESCRIPTION OF PREFERRED SAMPLING AND PRESERVATION PROCEDURES

This is a relatively simple procedure. Acid wash screw-capped polythelyene containers (approximately 300 ml capacity) by immersing in 1:1 nitric acid for ½ hour. Thoroughly rinse containers in distilled water followed by a final rinse with deionized distilled water. Allow containers to dry and then store in clean, polyethlene bags for transporting to the field. Prepare ice chest for field

sampling by spreading ice in plastic bags over the bottom of the chest. Rinse sample containers three times with sample and then fill container with sample and store in cooled ice chest for transporting to laboratory. After returning to the laboratory and within 24 hours after sampling, filter samples through a 0.45 μm Millipore filter and return sample to original container. Cap tightly and store in darkened cold room at 10°C. Perform hydride analyses within five days. Studies with sea water (Rasmussen, 1981) indicate that non-acidified samples can be stored at least several weeks for subsequent preconcentration and analyses for trace elements. Non-acidification allows effective buffer pH control of samples for the extaction method (Appendix A).

Precipitation of salt from samples with a very high TDS near supersaturation is likely whether samples are cooled (10°C) or kept at ambient temperature. The same sampling, handling and filtration procedure is therefore recommended for all samples. If salt precipitation is observed in a sample following filtration, the container and sample should be immersed in a 50°C water bath until the precipitate dissolves before removing aliquots for analyses. We observed only one sample out of 116 with evident salt precipitation when stored at 10°C.

VII. DRAINAGE AND EVAPORATION POND ANALYTICAL DATA

Appendix C contains a listing of mineral element concentrations measured in 116 drainage and evaporation pond water samples grouped

together, and in three different geological zones in the San Joaquin
Valley.

The ranges of concentrations of each element determined in separate
sample aliquots (116 samples) by different methods are shown below.

<p style="text-align:center">TABLE II.</p>

<p style="text-align:center">RANGES IN CONCENTRATIONS OF ELEMENTS IN SEPARATE</p>

<p style="text-align:center">SAMPLE ALIQUOTS OF 116 EVAPORATION POND WATER SAMPLES</p>

In 1+9 Sample Dilution		By Extraction Method		By Hydride Generation	
Element	Range	Element	Range	Element	Range
	mg L^{-1}		mg L^{-1}		mg L^{-1}
Ca	<0.5–911	Fe	.003–.144	Se	<.001–2.06
Mg	21–8920	Mn	<.001–.79	As	.001–4.49
Na	1590–76000	Cu	.001–.014	Sb	ND
K	<5–230	Zn	.002–.027	Bi	ND
P	<0.5–2.35	Pb	<.003–.10	Ge	ND
Si	<0.10–30	Cd	<.001–.001	Te	ND
B	3.2–392	V	.003–.544	Hg	ND
Ba	<0.05–.10	Ni	.001–.027		
Sr	<0.1–33	Cr	<.001–.008		
Li	<0.1–4.0	U	.011–9.9		
Al	<0.3–1.7	Se^{+4}	.010–.070		
Mo	<0.08–24	As^{+3}	<.001–.055		
Be	ND*	Ga	ND		
Sc	ND	Au	ND		
Ti	ND	Hg	ND		
Ag	ND	Sn	ND		
		Sb	ND		
		Bi	ND		
		Te	ND		

*ND, not detected

Elements in drainage and pond water samples can be divided into three groups based on concentrations and concerns for their potential environmental impacts. Boron, molybdenum, vanadium, uranium, selenium, and arsenic are trace elements of primary environmental concern. One and/or more of these elements occur at relatively elevated levels in most samples. Gallium, gold, mercury, tin, antimony, bismuth, tellurium, beryllium, scandium, titanium, germanium and silver comprise another group of elements, some of which are of concern, but were not detected. Four of these elements, i.e., Hg, Bi, Te and Sb, were not detected by either hydride or the extraction method which adds validity to the methods. The remaining elements, except the major cations (Ca, Mg, Na, and K) occur at relatively low concentrations in most samples. Of these, P and Al values were measured near the detection limits in a high salt matrix and are therefore of questionable accuracy.

Several elements exhibit distinctly different concentrations within different geological zones as shown on data sheets in Appendix C. A more complete discussion of the significance, distribution and associations of U, V and Mo with salinity is found in Appendix B.

VIII. VALIDATION OF RESULTS

Purified Salton Sea water was spiked with trace element standard solutions and extracted as described in the method (Appendix A). Concentrations of spiked trace elements and major elements in test solutions approximated concentrations in saline water samples. Table 2 in

the extraction method lists the extraction efficiencies ranging from 90-102% for the trace elements listed. This is presented as a basis for validation of sample analyses.

Eleven pond water samples were selected by the RWQCB for duplicate and spiked recovery tests. Data showing the results are in Appendix C. Duplicate analyses show acceptable results for most elements except Al, as are spiked recoveries except for chromium and lead. Suspended colloidal clay in unfiltered pond waters will go through the nebulizer of the ICP, resulting in variable concentrations for iron, aluminum and silicon. The overall results are better than expected since samples were not filtered and were stored several months after being spiked with very low concentrations. Jenne and Tuoma (1975), Florence and Battey (1975), and Hayase et al. (1975) emphasize the magnitude of active chemical and physical processes affecting the solubility of trace elements in unfiltered water.

The following tests were made and analyzed statistically to provide additional evidence for the accuracy and reliability of the analyses.

Twenty-two pond water samples were randomly selected, re-analyzed by the extraction method, and the results compared with earlier analyses by regression analyses. For extractable elements with concentrations above estimated detection limits, R^2 values (U .98-.99, V .996) show good agreement.

Values for Ca, Mg, Na, K and B were measured in 22 randomly selected samples and compared by regression analysis with values reported by the RWQCB. The R^2 values (Ca .965, Mg .973, Na .957, K .918, and B .956) reflect good agreement.

Twenty-two samples were randomly selected and concentrations of Si, Sr, B and Mo measured in 1+9 and 1+99 dilutions at different times, and the results compared by regression analysis to assess the magnitude of salt matrix effects. This approach assumes a linear instrument response for elements present above the detection limit within the range of dilutions. A nonlinear response, indicated by low R^2 values, is therefore attributed to salt matrix effects. The R^2 values (Si .943, Sr .984, B .925, Mo .934) indicate acceptable results. However, higher R^2 values are probably attainable by filtration of samples and closer matrix matching of samples and standards.

Nineteen samples were randomly selected, analyzed at different times by hydride analysis, and the results compared by regression analysis. The following R^2 values (se .972, As .998) show good agreement for Se and As measurement.

All samples were analyzed for both uranium and molybdenum by independent laboratories and the results compared with our analyses using regression analysis. The R^2 values (U .937, Mo .971) show generally good agreement.

A comparison of selenite values measured by the extraction method with total Se measured by hydride generation in a limited number of samples gave an R^2 value (.997) indicating a high positive correlation. Arsenite concentrations, as measured by the extraction method, were too low in most samples to make a similar comparison. These observations suggest that the extraction method has application to speciation studies

of Se and As. Relatively low fractions (<1/50) of total Se in pond waters were measured in a reduced (selenite) state.

Computer plots for all R^2 values quoted above are listed with the data tables in Appendix C.

Our laboratory follows a QA/QC program (see Appendix E) and participates in the University of California Salinity/Drainage Task Force and U.S.G.S. Round Robin Test Programs.

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Appendix A.   Extraction Method

Chelation and Solvent Extraction of Trace Elements from Saline Waters for Analysis by Inductively Coupled Plasma Optical Emission Spectroscopy

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Synopsis:

Preconcentration of Fe, Mn, Cu, Zn, Cd, Pb, V, Mo, Ni, Co, Cr, Tl, Ga, Au, U, Hg, Se, As, Sn, Sb, Bi and Te from saline water buffered with ammonium acetate to pH 5.0 is described using multielement chelation with ammonium pyrrolidine dithiocarbamate extracted into chloroform. Extract residues were taken up in dilute nitric acid solution for analysis by simultaneous multielement inductively coupled plasma-optical emission spectroscopy. Recovery percentages of elements at low $\mu g\ l^{-1}$ levels in spiked, purified Salton Sea water samples ranged from 90-102%. Saline agricultural drainage and evaporation pond water samples from the San Joaquin Valley, California, were analyzed by this method with accuracy of uranium and molybdenum analyses determined by comparison of results with independent laboratories using other methods.

Direct determination of low µg l^{-1} concentrations of many trace elements by inductively coupled plasma optical emission spectrometry (ICP-OES) in saline waters is not feasible due to insufficient instrumental sensitivity and/or interferences from a highly saline matrix. Liquid-liquid extraction,[1] coprecipitation,[2] chelating ion-exchange,[3] solvent evaporation,[4] hydride generation,[5] and chelation-solvent extraction[6] have been used for preconcentration. However, none of the methods have been fully adapted for simultaneous multielement analyses by ICP-OES using direct aqueous nebulization. A simple, rapid and reliable method, compatible with ICP-OES, is desirable.

Dithiocarbamates have been used to complex many metals for extraction into an organic phase with high distribution ratios.[6-9] A typical structural formula for a metal (M) complex of ammonium pyrrolidine dithiocarbamate (APDC) is shown here.
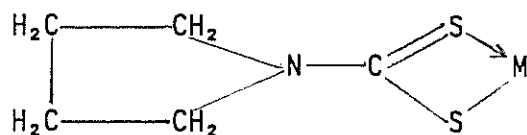
A multielement preconcentration method with large enrichment factors by extraction of APDC metal complexes into chloroform is reported in this paper.

The method is relatively simple, rapid and adaptable to aqueous pneumatic nebulization with ICP-OES.

Experimental

Apparatus

A Jarrell-Ash Atomcomp 800 series spectrometer with computer-controlled background correction including spectral line overlap correction and other timing and standardization functions was used. Mass flow controllers were used to control argon gas flow to a cross flow nebulizer and torch. A combination constant temperature water bath and pump were used to circulate distilled water through the RF coil. Spectrum line photographic records were made on a Wadsworth spectrometer which operated simultaneously with a single channel .5 M Ebert spectrometer and an 800 series spectrometer. A peristaltic pump controlled sample solution flow to the nebulizer.

Table 1 lists the wavelenths and estimated detection limits for elements analyzed by ICP-OES instrumentation in our laboratory. Operating conditions are listed below:

Argon flow

Coolant, 14 1 min^{-1}

Sample, .5 1 min^{-1}

Plasma, 0 1 min^{-1}

Argon pressure to nebulizer, 552 kPa

Nebulizer type, cross-flow

Integration time, 15 s on line, 15 s background

Incident power, 1.25 KW

Reflected power, <10 W

Observation height, 13 mm above coil

Sample aspiration rate, 1.5 ml min^{-1}

Teflon (Fisher Scientific) separatory funnels (250 and 500 ml capacity) and beakers (30 ml capacity) were used for solvent extractions and evaporation of combined chloroform extracts. Teflon (TFE) and Teflon (FEP) are polytetrafluorethylene and fluorinated ethylene-propylene, respectively, products of E. I. duPont deNemours and Co., Wilmington, Delaware, USA. However, the authors make no recommendations of any supplier source of these nor any other apparatus nor products used in this study.

Reagents:

Standards were prepared from stock solutions (2,000 mg l^{-1}) made from high purity chemicals supplied by SPEX Industries, Inc., Box 798, Metuchen, NJ 08840, USA, or Johnson Mathey an Co. Ltd., 73/83 Halton Garden, London, E.C.I.

Standards and stock solutions were prepared in purified diluted (<1%) HNO$_3$, HCl, or deionized distilled water (DIDW) and were stored in clean polyethylene containers. Working standards of lower concentrations were prepared fresh weekly from stock solutions and emission intensities of calibration standards checked at the beginning of daily sample runs.

Deionized distilled water was prepared by passing distilled water through an exchange resin column (IonXChanger Research No. 1506-35 supplied by Cole Parmer Instrument Co., 7425 N. Oak Park Avenue, Chicago, IL 60624, USA). The purity of DIDW was checked

frequently by running blanks and observing emission intensities. DIDW was used in preparation of all standards and for other laboratory uses including a final rinse when cleaning laboratory ware.

Chloroform of high purity (Fisher Scientific Optima C297-4) was used. Reagent-grade acids (nitric, acetic and 6 mol hydrochloric) and ammonium hydroxide were purified by distillation from a 1-liter round-bottom flask attached to a Teflon condenser.

Ammonium pyrrolidine dithiocarbamate (APDC) was prepared as follows[10] from high purity pyrrolidine, ethyl alcohol, carbon disulfide and ammonium hydroxide. A 500 ml reaction beaker was immersed in crushed ice and each addition of reagent made slowly and with stirring to avoid a violent reaction. Forty-five ml of pyrrolidine were added to 100 ml of ethyl alcohol in a cooled 500 ml beaker. After 30 minutes, 30 ml of carbon disulfide were added slowly followed by 75 ml of 8 N NH_4OH. After about 1 hour white crystals of APDC were suction-filtered using a sintered glass filter and washed with a limited volume of ice-cold ethyl alcohol. APDC was air-dried on the filter and transferred to a polyethylene container and stored in a refrigerator. A 3% (m/v) solution (500 ml) was prepared with DIDW, the pH adjusted to 5.0 with dilute acetic acid, and then 250 ml portions were extracted five times with 10 ml portions of chloroform to remove trace metal impurities. APDC remained stable for several weeks stored in a refrigerator in a polyethylene container.

A one mol ammonium acetate buffer solution (500 ml) was prepared from reagent grade chemical and the pH adjusted to 5.0 with

dilute acetic acid and/or ammonium hydroxide. Each 250 ml portion was extracted five times with 10 ml portions of chloroform to remove trace element impurities. The chloroform extracts were discarded and the solutions of ammonium acetate stored in polyethylene containers.

Sample Collection

One hundred sixteen agricultural drainage and evaporation pond water samples from the San Joaquin Valley were collected in June 1988 by personnel of the Central Valley Region Water Quality Control Board. These samples were collected for testing of a proposed chelation solvent extraction method for trace element analysis of saline waters. Samples were not filtered nor acidified and had been stored at room temperature about three months before we received them. There was evident suspended and precipitated material in most samples. The actual concentration of the original low level trace element content of these samples is therefore questionable.

Coprecipitation, container adsorption or release of trace elements and biological volatilization may have caused temporal changes in the trace element content of samples. Nevertheless, the exercise of analyzing these samples by the preconcentration method described was invaluable.

Procedure

Samples

A (1+9) and a (1+99) dilution of each saline water sample were analyzed directly by ICP-OES to identify samples containing relatively high concentrations of trace and major elements. Sample aliquots for extraction were pre-adjusted to pH 5.0 with acetic acid or ammonium hydroxide to insure accurate buffer pH control during extraction. An aliquot (10-200 ml, depending on the trace element content) of a saline water sample was transferred to a 250-ml Teflon separatory funnel held upright in a funnel rack. Ten ml of purified 1 mol ammonium acetate solution (pH 5.0) were added, followed by 5 ml of purified APDC. After 10 minutes, 10 ml of chloroform were added and the separatory funnel shaken briefly by hand, inverted and gas pressure released by turning the stopcock open momentarily. This was repeated until no further pressure developed. The funnel was transferred to a horizontal mechanical shaker. After shaking the separatory funnel and contents vigorously for 3 minutes, it was removed to an upright position, and time allowed for phases to separate before the chloroform layer was drained off slowly into a 30-ml Teflon beaker.

Another 5 ml of APDC solution was added and the separatory funnel (uncapped) was transferred to a microwave oven and the contents heated to incipient boiling (approximately 1.5 minutes

on high). The separatory funnel was removed from the microwave

oven and allowed to cool to room temperature (approximately 20

minutes) before recapping and extracting with another 10 ml of

chloroform. This chloroform extract was combined with the previous

extraction. Another 10 ml of chloroform were added (no APDC),

extracted and combined with the previous extractions. Any visible

water droplets in each chloroform extract were removed by drawing

into a disposable polyethylene dropper and adding back to the

aqueous phase. Occasionally highly saline samples containing high

levels of silica formed an emulsion layer which was difficult to

separate. In this case we diluted a smaller sample aliquot with

DIDW for analyses. The combined volume of chloroform was slowly

evaporated to dryness on a temperature-controlled hot plate at

<50°C. A half ml of concentrated nitric acid was added dropwise

(reacts vigorously) and evaporated to near-dryness at <50°C. Three

ml of a 1% solution of HNO_3 were added and analyzed by ICP-OES.

Test solutions

In order to test the APDC solvent extraction method in a highly

saline background, Salton Sea water was used as the matrix. The

water was first filtered through a No. 42 Whatman filter paper to

remove the suspended particles. Two hundred ml portions of water

were purified using the APDC-chloroform extraction method after they

were buffered at pH 5.

Purified Salton Sea water (20 ml diluted to 100 ml with DIDW) was spiked with trace element standard solutions and extracted as described above to measure extraction efficiency. Trace element concentrations in test solutions extracted varied between 10 and 120 µg l^{-1} for different elements depending on their sensitivity when measured by ICP-OES. Recovery tests for a range of concentrations for each element were not performed since Cresser[11] showed that the extractability for any element is independent of its solution concentration. Concentrations of trace and major elements in test solutions approximated concentrations in saline water samples.

Results and Discussion

Table 2 shows the emission intensity values and statistical significance of standard trace element solutions analyzed by ICP-OES compared to aliquots treated by the chelation-solvent extraction procedure described above. Extraction efficiencies range between 90 and 102% for 22 elements listed in Table 2. The extraction efficiencies shown for gold and antimony are for standard solutions of these elements adjusted to pH 1 with HCl (no ammonium acetate added) and extracted as described for other elements. Lower extraction efficiencies (50-75%) for these elements in an ammonium acetate buffered solution (pH 5.0) are undoubtedly due to lower solubility of these elements at the higher pH. A separate sample

aliquot must therefore be analyzed for these elements to achieve the higher recovery percentages.

Other elements reported by Lankanen[6] to be extractable by APDC chelation are palladium, indium and tungsten. Malissa and Schöffman[10] identified colors of APDC precipitates of iridium, niobium, osmium, platinum, rhodium and ruthenium, thus suggesting that these elements are also extractable. We have not tested the extractability of these elements except for W^{+6} which was not extracted. Th^{+4} was tested but did not extract.

One hundred sixteen saline drainage and evaporation pond water samples were analyzed by the chelation solvent extraction method described herein. Bradford et al.[12] reported unusually high levels of uranium, vanadium and molybdenum in these waters. Initial measurements of high uranium in samples were unexpected and confirmed by examination of photographic records of spectrum lines from ICP-OES analyses of samples. Table 3 shows the range and mean concentrations of trace elements within three different geological zones from which the samples were collected.

All samples were analyzed for uranium by an independent laboratory using a fluorometric method and compared statistically with the authors analyses using solvent extraction and ICP-OES. The following regression equation shows good agreement between the two methods: U (fluorometric) = U (solvent of extraction) x 1.018 - 0.0451.

High Mo content, especially in sample extracts, caused spectral interferences on lines of other elements, especially on the Zn 206.0

nm spectrum line. Although computer correction factors were used to
compensate for such interferences, the factors ceased to be reliable
at high concentrations of an element where the emission intensity
vs. concentration became nonlinear. Alternate solutions were to
install another Zn detector on a different spectrum line, use smaller
sample aliquots to reduce the Mo content or compare Mo values deter-
mined on different sample dilutions analyzed directly by ICP-OES
with values determined by an independent method. The latter alter-
native proved successful. We found good agreement between Mo
determined in a (1+9) sample dilution analyzed by ICP-OES compared
to values obtained by an independent laboratory using AAS, as shown
by the following regression equation: Mo (AAS) = Mo (solvent
extraction) x .9575 - .0249.

Analyte Species

The valence of metals in compounds used to prepare standards are
shown in Table 2. Only with selenium and arsenic were other valen-
ces of these elements tested. Se^{+6} and As^{+5} did not extract so the
method has the advantage of application for speciation measurements
of arsenic, selenium and possibly other elements. On the other
hand, it may be considered a disadvantage to be able to measure only
one species when both are present in solution.

Dissolution of Chelate Residue

A critical step in the procedure which makes possible the
analyses of extract residues in solution by conventional pneumatic

nebulization with ICP-OES is the dissolution of the residue

following evaporation of chloroform by nitric acid. Lakanen[8]

prepared pyrrolidine dithiocarbamaic acid in chloroform and

performed multiple trace element extractions from soil extracts.

He muffled the extract residues and analyzed the ash spectrochemi-

cally. We experimented with his method but found it unsatisfactory

for use with pneumatic nebulization because the relatively high

carbamate chelate residue did not go into an aqueous acid solution

and/or caused instability of the plasma. Attempts with low tempera-

ture oxidation of the residue were unsatifactory. Sugiyama et al.[8]

used 2-ethylhexyl acetate as an organic solvent to extract carbamate

chelates and nebulized the organic phase directly into ICAP-OES.

We were able to nebulize 2-ethylhexyl acetate successfully after

major changes in the RF power, gas flow and other parameters. How-

ever, a major problem developed later when we attempted to return

to pneumatic nebulization with aqueous solutions. Traces of solvent

remaining in the nebulizer assembly prevented ignition of the plasma

and necessitated complete removal and cleaning of all components.

The method has merit if instrumentation is dedicated to nebulization

of 2-ethylhexyl acetate. Our next effort was to develop chelates of

trace metals by the addition of water soluble APDC to samples,

followed by their extraction with chloroform. This proved success-

ful, as did the dissolution of the chelate residue with concentrated

nitric acid. The final solution was clear and stable in the plasma.

High temperature evaporation of chloroform and nitric acid must be

avoided to prevent the formation of insoluble residues.

Selection of Organic Solvent

Chloroform was selected because of its ready availability, low cost
and relative purity. It is also relatively insoluble (about 1% in
water) and has moderate volatility.

Effect of pH and Reagent Concentration on Extraction of Trace Elements

Several studies with carbamate chelates[6-10] have shown that most
elements listed in Table 2 are extractable over a wide pH range from
1 to 10. However, efficiency of extraction drops above pH 6 and
below pH 4.7 for different elements. Lankanen[6] observed that the
lower pH limit for quantitative extraction of manganese was 4.6,
that extractability of Mo, Sn and V dropped above pH 6.0, and that
Au and Sb were best extracted at pH 1.0. Cresser[11] used equilibrium
equations to develop mathematical distribution ratios which he con-
cluded are highly dependent on hydrogen ion and reagent concentration,
but independent of element concentrations in solvent extraction
systems. We selected pH 5.0, buffered with 1 N ammonium acetate
as a probable mid-range optimum pH, with two 5 ml additions of 3%
(m/v) APDC to give high extraction efficiencies as shown in Table 2.
If samples contained unusually high concentrations of analyte
species, even higher concentrations of chelate reagent were
required. To indicate the magnitude of insufficient reagent
concentrations, we observed a reduction from 90 to 60% recovery of
uranium when two 3-ml additions of 2% APDC were used compared to two
5-ml additions of 3% APDC.

Organic Phase Colors

Several elements listed in Table 2 lend typical colors to the organic phase. As, Cd, Hg, Pb, Sn, Se, Te, Tl, Zn and Ga complexes of APDC in chloroform are essentially non-colored, Ag and Sb yellow-white, Au and Cu brown, Co green, Ni grey-green, Cr grey-blue, Fe black, Mn red-black, and Mo redviolet. The complete disappearance of colors in the solvent phase with subsequent extractions was a good visible indication that extraction was complete. Malissa and Schöffman[10] identified similar colors of carbamate precipitates of different metals.

Temperature Effect on Extraction Efficiency

Mansell and Emmel[9] observed increased extraction efficiency of Cr by APDC in solutions heated to near boiling compared to room temperature. Our tests also showed increased recovery of tin and no apparent decrease in extraction efficiency of other elements. Since heating was readily accomplished by placing the separatory funnel and contents in a microwave oven for a short time we included this step in the procedure.

Kinetic Effects

Time and vigor of shaking of aqueous and organic phases must be sufficient to give high extraction efficiencies. We modified a conventional horizontal laboratory shaker by increasing the pulley drive ratio, thus increasing the vigor of shaking comparable to fast wrist action. Shaking for three minutes was accepted as a minimum

time and gave good extraction efficiency for the elements listed in Table 2.

Salting Out Effects

Matkovich and Christian[13] studied a large number of compounds and conclude that calcium and magnesium chloride added to the aqueous phase decreased the solubility of an organic solvent by a salting out effect. This suggests that solvent extraction is more efficient in samples containing a high salt content.

Potential Interferences

It is assumed when using a proposed extraction method that extraction and distribution ratios are constant for samples and test standards, and that all of an analyte species is available for complex formation and extraction.

The presence of species in samples capable of forming complexes with analyte species is a significant source of error. Lakanen[6] reported interference by phosphate on separation of iron, citrate on gallium and molybdenum, lactate on molybdenum, and oxalate on gallium and vanadium. Reducing solutions (.1% hydroquinone, 1% hydroxylamine hydrochloride) did not interfere, but 0.5% to 1% H_2O_2 prevented the extraction of several metals by pyrrolidine dithiocarbamic acid in chloroform.[6] Most of these interferants are destructable by vigorous wet oxidation methods.

Sources of Contamination

Sources of contamination are too numerous to list. The reader is referred to a monograph on contamination control in trace element analyses by Zief and Mitchell[14] and to Cresser's publication.[11]

All laboratory ware was cleaned with a mild detergent, rinsed and soaked 20 minutes in 1 N HNO_3, rinsed with distilled water and then with DIDW. Polyethylene gloves were worn when handling laboratory ware and making extractions. Extraction operations were performed in a fume hood to minimize contamination of samples and prevent exposure of laboratory personnel to toxic fumes of chloroform.

The authors observed mercury contamination $(0.1 - 0.2$ mg $1^{-1})$ in reagent grade hydrochloric acid while running 6 N HCl blanks through a continuous flow hydride generation accessory with ICAP-OES. We now routinely treat concentrated reagent grade hydrochloric acid to remove mercury by passing it through a 50 ml buret filled with 1-X8 anion exchange resin (100-200 mesh).

Losses of Trace Elements

Solution samples are especially vulnerable to trace element losses due to adsorption on the container walls and/or contamination from the container material. These effects become more significant at lower concentrations near detection limits. Different container materials exhibit different effects. Not all elements react the same. A few examples are of interest.

Struempler[15] reported that of the three elements Ni, Cd and Zn, only Ni was consistently adsorbed on polyethylene. Robertson[16] observed losses of indium, iron, silver, cobalt, rubidium, scandium, and uranium from samples stored in polyethylene containers at pH 8 and only scandium and uranium were lost when the solution was acidified to pH 1.5.

Acknowledgement

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Table I. ICAP-OES wavelengths and estimated** instrumental detection limits.

Element	Wavelength (nm)		Estimated detection limit (mg/L)
Aluminum	308.21		0.03
Arsenic	193.69		0.001*
Antimony	206.83		0.001*
Barium	493.40		0.002
Beryllium	234.86		0.0005
Boron	249.67	II	0.005
bismuth	223.06	II	0.001*
Cadmium	228.80	II	0.004
Calcium	393.36		0.005
Calcium	317.80		0.050
Chromium	267.71		0.002
Cobalt	228.61		0.005
Copper	324.75		0.010
Gold	242.80		0.005
Germanium	199.82		0.001*
Iron	259.94		0.005
Lead	220.35		0.020
Lithium	670.70		0.005
Magnesium	279.55		0.020
Manganese	257.61		0.005
Mercury	253.65		0.001*
Molybdenum	202.03	II	0.008
Nickel	231.60		0.010
Potassium	766.40		1.0
Phosphorus	214.91		0.050
Selenium	196.02		0.001*
Scandium	341.38		0.001
Silicon	251.61		0.010
Silver	328.06		0.005
Sodium	588.90		0.20
Strontium	421.50		0.008
Tellurium	214.20	II	0.001*
Thallium	190.86	II	0.100
Tin	284.00		0.100
Titanium	334.90		0.010
Uranium	385.96		0.20
Vanadium	292.40		0.010
Zinc	206.20	II	0.005

II second order lines
*   continuous hydride system with ICAP
** detection limits vary with sample matrix; detection limit is defined
    as the concentration equivalent to a signal due to the analyte, which
    is equal to three times the standard deviation of a series of 10
    replicate measurements of a zero calibration blank.

TABLE 2. EMISSION INTENSITIES OF STANDARD TRACE ELEMENT SOLUTIONS
          COMPARED TO ALIQUOTS TREATED BY CHELATION SOLVENT
          EXTRACTION AND ANALYZED BY ICAP-OES.

	STANDARD[1] SOLUTIONS	EXTRACTED[1] ALIQUOTS	PERCENT RECOVERY
Arsenic^{+3} (1)	4493±65	4590±17	102
Antimony^{+4} (1)	16,097±591	16,244±445	101
Bismuth^{+3} (4)	61,000±435	58,133±305	95
Cadmium^{+3} (1)	87,200±200	80,233±152	92
Chromium^{+3} (1)	50,966±750	49,266±1059	97
Chromium^{+6} (1)	52,033±451	49,266±1240	95
Cobalt^{+3} (1)	395,000±1734	385,333±2080	98
Copper^{+2} (1)	19,033±153	19,566±550	103
Gold^{+3} (1)	31,666±960	33,166±709	104
Gallium^{+3} (8)	120,666±2082	117,666±5507	98
Iron^{+3} (1)	55,233±404	63,400±872	114*
Lead^{+2} (4)	108,000±999	105,333±2309	98
Manganese^{+2+3} (1)	111,333±577	109,333±1154	98
Mercury^{+2} (4)	42,666±472	42,000±655	98
Molybdenum^{+6} (1)	52,666±115	51,700±346	98
Nickel^{+2} (1)	38,100±173	37,266±152	98
Selenium^{+4} (1)	7973±120	7946±11	100
Tellurium^{+4} (1)	5600±138	5640±123	101
Thallium^{+1} (4)	93,433±1914	89,000±754	95
Tin^{+2} (4)	49,600±99	49,866±1242	101
Uranium^{+6} (12)	13,933±378	12,466±115	90
Vanadium^{+5} (1)	22,700±346	22,266±115	98
Zinc^{+2} (1)	95,000±1411	96,433±3156	101

*Iron contamination (about 100 ug L^{-1}) from combined reagents is
 indicated by the higher intensity value in extracted aliquots.
 This, however, is only significant at low sample concentration
 ratios, since at higher concentration (100X), for example, the
 blank correction would be 1 ug L^{-1}. A reagent blank was processed
 with each set of samples to correct for contamination.

( ) mg L^{-1} concentrations of standard solutions

[1] analyzed and/or extracted in triplicate.

Table 3. Trace element concentrations in 116 agricultural drainage and evaporation ponds of the San Joaquin Valley of California.

	Alluvial fan		Basin rim		Lakebed	
	Range	Mean	Range	Mean	Range	Mean
	----------mg/L----------					
Al	.00-1.7	.48	.00-1.6	.32	.00-1.8	.40
As	.002-.020	.007	.001-.132	.031	.013-4.490	.364
B	6.0-333	80	3.6-203	45	3.3-392	32
Ba†	.00-.10	.016	.00-0.05	.01	.00-.04	.01
Cd†	.00-.001	.00	.00-.00	.00	.00-.00	.00
Cr†	.00-.01	.002	.00-.01	.001	.00-.00	.00
Cu†	.003-.014	.008	.001-.012	.005	.001-.012	.005
Fe†	.003-.041	.014	.004-.144	.034	.005-.056	.019
Li	.00-1.7	.540	.00-1.15	.073	.00-4.1	.349
Mn†	.00-.025	.007	.004-.685	.120	.00-.793	.041
Mo†	.061-12.7	2.07	.117-2.21	.628	.138-22.7	2.86
Ni†	.001-.012	.005	.001-.016	.005	.00-.027	.005
P	.00-.434	.090	.00-2.35	.402	.00-1.70	.432
Pb†	.00-.035	.003	.00-.007	.002	.00-.10	.005
Se*	.003-2.06	.451	.0001-.0124	.002	.000-.061	.0084
Si	.265-26.7	5.09	.374-23.5	11.5	.075-30.0	9.62
Sr	4.5-32.8	13.7	1.34-21.5	6.22	.063-20.1	3.84
U†	.075-2.16	.421	.011-.499	.183	.04-9.9	.896
V†	.003-.071	.029	.004-.096	.030	.004-.544	.087
Zn†	.00-.036	.007	.002-.027	.008	.00-.08	.006

00. = < detection limit, which varies with sample concentration factor.

*analyzed by continuous flow hydride generation with ICP-OES (modified from Thompson et al. (5)).

† analyzed by chelation solvent extraction and ICP-OES.

It is significant that although all samples were analyzed for Co, Tl, Ga, Sn, Sb*, Bi*, Te* and Hg* by chelation solvent extraction and/or hydride generation, no positive values were measured above a low $\mu g\ L^{-1}$ detection limit.

APPENDIX B

REVIEW OF U, V AND Mo

Uranium, Vanadium, and Molybdenum in Saline Waters of California

G. R. Bradford,* D. Bakhtar, and D. Westcot

ABSTRACT

Analyses of saline water samples from large salt water bodies, agricultural drainage and evaporation ponds, and soil water extracts were used to determine the extent of elevated uranium (U), vanadium (V), and molybdenum (Mo) in agricultural environments of the San Joaquin Valley. Saline water samples and soil extracts were pretreated by chelation and solvent extraction to separate and concentrate, U, V, and Mo for analyses. Mean concentrations of U, V, and Mo were considerably elevated in agricultural drainage and evaporation ponds of the San Joaquin Valley compared to saline waters of Salton Sea and Mono Lake. Relatively high correlation coefficients were observed between U, Mo, and salinity.

T HE United States Geological Survey, in cooperation with the U.S. Fish and Wildlife Service and the U.S. Bureau of Reclamation, recently published the results of a detailed study of two National Wildlife Refuges (NWR) grouped within about 24 km (15 miles) of each other on the south side of Tulare Lake Bed, southern San Joaquin Valley (Schroeder et al., 1988). The purpose of the study was to determine if chemical contamination in drainage water from agricultural irrigation pose a threat to wildlife on or near the NWR, and to ascertain if more detailed studies are warranted. They found elevated levels of U, V, Mo, and other trace elements in an agricultural evaporation pond near Kern NWR. They identified U as high (250–360 μg/L) in pond water with bottom material from the same pond containing 6.6 + 3.7 mg/kg. Uranium was determined by a direct fluorometric method with the authors' comment that "Sensitivity of the method is typically reduced in saline waters by quenching of U fluorescence; hence, reported concentrations should be considered minimum estimates" (Schroeder et al., 1988).

Deverel and Millard (1988) suggest that Mo, V, and other trace elements are probably present as dissolved oxyanions in alkaline waters of the western San Joaquin Valley. Uranium is an oxyphile element often concentrated in petroleum and associated brines (Rankama and Sahama, 1950).

The objective of the present study was to provide a preliminary assessment of U and geochemically associated V and Mo distribution in saline waters and soil solutions of the San Joaquin Valley, CA.

MATERIALS AND METHODS

Study Area

The San Joaquin Valley constitutes the southern two-thirds of the Central Valley of California and represents approximately 3.4 million ha of valley floor. The following

G.R. Bradford and D. Bakhtar, Dep. of Soil and Environ. Sci., Univ. of California, Riverside, CA 92521, and D. Westcot, California Regional Water Quality Control Board, Central Valley Region, 3443 Routier Road, Sacramento, CA 95827-3098. Supported by State of California Water Quality Control Board. Received 4 Oct. 1988. *Corresponding author.

description of the Central Valley is taken from Schroeder et al. (1988). The Central Valley is a northwestward-trending asymmetric trough bounded by granitic, metamorphic, and marine sedimentary rocks, and filled with as much as several kilometers of sediment. Near the close of the Late Cretaceous Epoch, tectonic movements elevated the Coast Ranges on the west side of the Valley and created the ancestral Central Valley as a restricted trough of deposition lying between the emerging Coast Ranges and the Sierra Nevada to the east.

Within the San Joaquin Valley are 27 salt water evaporation ponds of varying sizes up to 720 ha (1800 acres), which are fed by subsurface drainage from surrounding irrigated lands (Westcot et al., 1988).

The California Water Atlas, 1978–79 (Kahrl, 1979) gives the following description of two large salt water bodies. Salton Sea is an unnatural body of water formed when a man-made diversion channel from the Colorado River flooded out of control in 1905 and filled the Salton Sink in the Imperial Valley. It covers about 1036 km² and has been maintained by surface inflow from saline irrigation water. Mono Lake is a saline body of water covering about 260 km² to the east of the Sierra Nevada.

Saline water samples were collected from 62 agricultural drainage waters and evaporation ponds in the San Joaquin Valley. Samples were collected from two cells of Kesterson Reservoir in the San Joaquin Valley and from Salton Sea and Mono Lake.

Nine surface benchmark soils collected from the west side of the San Joaquin Valley for an earlier study by Bradford et al. (1971) were analyzed as part of the current study.

Soil extracts (1:1) and water samples were buffered by the addition of ammonium acetate and U, V, and Mo chelated by the addition of an aqueous solution of ammonium pyrrolidine dithiocarbamate. Samples were then extracted three times with chloroform and the extracts combined and evaporated to dryness. The residue was then dissolved in nitric acid, evaporated, and made to a small volume for analysis with inductively coupled argon plasma optical emission spectroscopy (ICAP-OES).

RESULTS AND DISCUSSION

Before the report of U in an evaporation pond in the San Joaquin Valley by Schroeder et al. (1988) was printed, and while we were engaged in laboratory experiments to develop and test a chelation solvent extraction technique to remove and concentrate numerous trace elements from high salt waters, we observed a distinctive amber color develop in the solvent phase of evaporation pond water samples from the San Joaquin Valley. The amber color was not observed in water samples from the Salton Sea and Mono Lake. Subsequent analyses of the solvent phase with (ICAP-OES) revealed elevated levels of U, Mo, and V. High concentrations of U were unexpected, so we repeated the extraction and analyses of the pond water samples and included a blank spiked with U. Spectra were recorded on film during analyses with ICAP-OES. A light amber color appeared in the solvent phase of both samples and the U-spiked blank.

A comparison of spectra from samples and the spiked blank showed perfect matching of position and relative intensity of numerous spectrum lines of U. The sample containing the highest U was diluted 10×

APPENDIX C

DATA TABLES AND GRAPHS

Data file **116PONDS**
Title: CHEMICAL ANALYSES OF POND WATERS OF WESTERN SAN JOAQUIN VALLEY,CA

Function: PRLIST
Data case no. 1 to 30
Without selection

LIST OF VARIABLES

VAR	TYPE	NAME/DESCRIPTION
1	text 12	FIELD NUMBER
2	numeric	GEOLOGICAL ZONE
3	text 8	GEOLOGICAL ZONE
4	numeric	LAB. NUMBER
5	numeric	pH
6	numeric	EC (dS M^{-1})
7	numeric	Al (mg L^{-1})/direct
8	numeric	As (ug L^{-1})/hydride
9	numeric	B (mg L^{-1})/direct

CASE NO.	1	2	3	4	5	6	7	8	9
1	ALT-01	1	ALLUVIAL	179	8.20	25.5	1.21	3.0	45.800
2	ALT-02	1	ALLUVIAL	180	8.80	27.1	0.00	4.1	46.400
3	ALT-03	1	ALLUVIAL	181	8.90	34.2	0.00	5.5	59.000
4	ALT-04	1	ALLUVIAL	182	8.40	96.4	0.95	16.2	333.000
5	ALT-05	1	ALLUVIAL	183	8.70	33.4	0.00	3.3	62.500
6	ALT-06	1	ALLUVIAL	184	8.60	51.5	0.37	7.9	111.000
7	ALT-07	1	ALLUVIAL	185	8.40	29.4	0.00	3.2	57.100
8	ALT-17	1	ALLKUVIA	84	8.80	73.0	0.00	9.6	129.000
9	ALT-18	1	ALLUVIAL	85	8.80	73.2	0.12	15.1	127.000
10	ALT-19	1	ALLUVIAL	86	8.70	97.9	0.00	18.8	204.000
11	ALT-20	1	ALLUVIAL	87	8.70	88.0	1120.00	19.9	171.000
12	HME-18	1	ALLUVIAL	165	8.90	69.6	0.00	9.6	125.000
13	ALT-22	1	ALLUVIAL	89	8.40	62.8	1.68	7.1	86.500
14	ALT-23	1	ALLUVIAL	90	8.40	47.8	1.24	10.5	84.800
15	BJG-04	1	ALLUVIAL	140	8.20	45.9	0.00	3.5	39.300
16	BJG-05	1	ALLUVIAL	141	7.40	33.0	0.65	2.3	27.000
17	BJG-06	1	ALLUVIAL	142	8.00	9.6	0.20	1.5	5.980
18	BJG-07	1	ALLUVIAL	143	7.40	13.7	0.79	2.1	8.690
19	BJG-08	1	ALLUVIAL	144	7.60	18.2	0.22	1.9	13.200
20	BJG-09	1	ALLUVIAL	145	7.20	23.4	0.45	1.9	16.700
21	BJG-10	1	ALLUVIAL	146	7.90	19.3	0.00	3.4	38.800
22	BJG-11	1	ALLUVIAL	147	8.00	20.3	1.18	3.8	40.900
23	HME-14	1	ALLUVIAL	81	8.80	35.0	1.09	4.0	67.000
24	HME-15	1	ALLUVIAL	82	8.10	18.0	0.07	2.8	35.900
25	HME-16	1	ALLUVIAL	83	8.90	36.2	1.09	6.7	73.600
26	HME-17	1	ALLUVIAL	164	8.30	42.6	0.00	9.0	70.400
27	EWJ-06	2	BASINRIM	105	8.00	23.1	0.33	6.1	29.000
28	BJG-01	2	BASINRIM	137	8.00	10.3	0.00	53.0	203.000
29	BJG-02	2	BASINRIM	138	8.70	41.0	0.00	3.3	38.100
30	EWJ-08	2	BASINRIM	107	8.00	19.8	1.08	5.0	41.200

Data file 116PONDS
Title: CHEMICAL ANALYSES OF POND WATERS OF WESTERN SAN JOAQUIN VALLEY,CA

Function: PRLIST
Data case no. 31 to 60
Without selection

LIST OF VARIABLES

VAR	TYPE	NAME/DESCRIPTION
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2	numeric	GEOLOGICAL ZONE
3	text 8	GEOLOGICAL ZONE
4	numeric	LAB. NUMBER
5	numeric	pH
6	numeric	EC (dS M^-1)
7	numeric	Al (mg L^-1)/direct
8	numeric	As (ug L^-1)/hydride
9	numeric	B (mg L^-1)/direct

CASE NO.	1	2	3	4	5	6	7	8	9
31	BY-01	2	BASINRIM	148	8.10	23.700	1.570	26.0	12.400
32	BY-02	2	BASINRIM	149	7.40	67.600	0.520	132.0	64.100
33	BY-03	2	BASINRIM	150	7.60	77.500	0.123	105.0	63.200
34	BY-04	2	BASINRIM	151	8.20	25.200	0.149	23.0	13.500
35	BY-05	2	BASINRIM	152	7.70	39.800	0.524	46.0	24.900
36	BY-06	2	BASINRIM	153	7.70	39.800	0.000	47.0	24.200
37	BY-07	2	BASINRIM	154	7.80	40.000	0.000	48.0	26.600
38	EWJ-01	2	BASINRIM	100	7.30	59.000	0.759	20.0	92.900
39	EWJ-02	2	BASINRIM	101	7.60	59.100	0.000	20.0	92.900
40	EWJ-03	2	BASINRIM	102	8.00	23.400	0.000	7.0	32.000
41	EWJ-04	2	BASINRIM	103	0.00	19.500	0.152	1.0	24.500
42	EWJ-05	2	BASINRIM	104	7.90	10.000	0.007	1.0	12.300
43	EWJ-21	2	BASINRIM	136	7.40	18.300	0.736	6.1	9.470
44	EWJ-07	2	BASINRIM	106	8.00	91.400	0.000	59.1	188.000
45	EWJ-15	2	BASINRIM	114	8.00	21.100	0.436	52.0	11.000
46	EWJ-09	2	BASINRIM	108	8.20	91.700	0.000	55.0	164.000
47	EWJ-10	2	BASINRIM	109	7.90	21.800	0.145	5.0	37.200
48	EWJ-11	2	BASINRIM	110	8.50	27.000	0.000	25.0	15.000
49	EWJ-19	2	BASINRIM	134	7.70	15.700	0.523	7.0	6.340
50	EWJ-13	2	BASINRIM	112	8.60	32.900	0.000	23.0	17.300
51	EWJ-14	2	BASINRIM	113	8.30	12.100	0.000	38.0	5.280
52	EWJ-18	2	BASAINRI	133	7.00	13.800	0.000	9.0	6.240
53	EWJ-16	2	BASINRIM	115	8.10	19.100	1.140	36.0	7.820
54	EWJ-17	2	BASINRIM	132	8.10	8.690	1.170	8.0	3.640
55	HME-11	3	LAKEBED	78	8.10	20.300	0.000	188.0	10.700
56	LRG-10	3	LAKEBED	125	8.70	5.780	0.000	128.0	3.460
57	LRG-18	3	LAKEBED	92	8.10	14.900	0.000	88.0	9.330
58	BY-15	3	LAKEBED	162	7.60	25.600	0.000	103.0	17.900
59	ALT-08	3	LAKEBED	186	8.40	21.800	0.581	291.0	24.600
60	ALT-09	3	LAKEBED	187	8.20	30.900	0.000	345.0	36.300

Data file **116PONDS**
Title: CHEMICAL ANALYSES OF POND WATERS OF WESTERN SAN JOAQUIN VALLEY,CA

Function: PRLIST
Data case no. 61 to 90
Without selection

LIST OF VARIABLES

VAR	TYPE	NAME/DESCRIPTION
1	text 12	FIELD NUMBER
2	numeric	GEOLOGICAL ZONE
3	text 8	GEOLOGICAL ZONE
4	numeric	LAB. NUMBER
5	numeric	pH
6	numeric	EC (dS M^-1)
7	numeric	Al (mg L^-1)/direct
8	numeric	As (ug L^-1)/hydride
9	numeric	B (mg L^-1)/direct

CASE NO.	1	2	3	4	5	6	7	8	9
61	HME-10	3	LAKEBED	77	8.50	36.1	1.17	66.4	22.800
62	ALT-11	3	LAKEBED	189	8.20	140.0	1.07	4490.0	392.000
63	ALT-12	3	LAKEBED	190	9.20	56.2	0.00	920.0	74.400
64	ALT-13	3	LAKEBED	191	8.70	108.0	0.84	3125.0	140.000
65	ALT-14	3	LAKEBED	192	8.30	17.4	0.11	536.0	13.700
66	ALT-15	3	LAKEBED	193	8.30	19.3	0.35	538.0	13.300
67	ALT-16	3	LAKEBED	194	8.10	28.2	0.85	968.0	20.300
68	By-08	3	LAKEBED	155	8.20	57.0	1.03	233.0	44.100
69	BY-09	3	LAKEBED	156	7.90	37.7	0.08	168.0	26.300
70	BY-10	3	LAKEBED	157	7.80	42.1	0.09	179.0	28.800
71	BY-11	3	LAKEBED	158	7.50	64.1	1.12	240.0	51.800
72	BY-12	3	LAKEBED	159	7.40	48.0	0.00	218.0	36.200
73	LRG-02	3	LAKEBED	117	8.60	8.8	0.14	145.0	5.280
74	BY-14	3	LAKEBED	161	7.60	33.8	0.55	140.0	25.100
75	LRG-04	3	LAKEBED	119	8.70	6.9	0.33	132.0	4.590
76	BY-16	3	LAKEBED	163	8.00	22.1	0.06	83.8	16.800
77	BY-17	3	LAKEBED	173	7.30	33.5	0.00	161.0	24.100
78	BY-18	3	LAKEBED	174	8.00	17.2	0.00	81.2	10.300
79	BY-19	3	LAKEBED	175	7.70	19.3	0.00	83.5	12.300
80	BY-20	3	LAKEBED	176	8.10	108.0	776.00	497.0	125.000
81	HME-19	3	LAKEBED	166	7.70	80.5	0.46	143.0	71.800
82	BY-22	3	LAKEBED	178	8.00	32.9	0.31	51.6	27.300
83	HME-01	3	LAKEBED	68	7.40	83.7	1.01	859.0	42.100
84	HME-02	3	LAKEBED	69	7.60	52.2	0.16	439.0	22.200
85	HME-03	3	LAKEBED	70	8.20	30.3	0.81	255.0	10.000
86	HME-04	3	LAKEBED	71	7.70	52.6	0.00	441.0	21.700
87	HME-05	3	LAKEBED	72	8.00	53.2	0.93	177.0	16.200
88	HME-06	3	LAKEBED	73	8.10	57.4	1.75	25.8	16.400
89	HME-07	3	LAKEBED	74	8.90	77.8	0.00	12.7	26.700
90	HME-08	3	LAKEBED	75	8.60	45.1	0.00	14.1	20.500

Function: PRLIST
Data case no. 91 to 116
Without selection

LIST OF VARIABLES

VAR	TYPE	NAME/DESCRIPTION
1	text 12	FIELD NUMBER
2	numeric	GEOLOGICAL ZONE
3	text 8	GEOLOGICAL ZONE
4	numeric	LAB. NUMBER
5	numeric	pH
6	numeric	EC (dS M^-1)
7	numeric	Al (mg L^-1)/direct
8	numeric	As (ug L^-1)/hydride
9	numeric	B (mg L^-1)/direct

CASE NO.	1	2	3	4	5	6	7	8	9
91	HME-09	3	LAKEBED	76	7.90	21.800	0.000	163.0	10.200
92	LRG-21	3	LAKEBED	95	8.40	72.000	0.167	354.0	49.600
93	LRG-06	3	LAKEBED	121	8.30	13.300	0.321	188.0	7.200
94	HME-12	3	LAKEBED	79	9.20	56.400	0.000	2600.0	57.600
95	LRG-24	3	LAKEBED	98	9.60	55.800	1.140	14.0	45.400
96	LRG-09	3	LAKEBED	124	8.90	5.930	0.441	132.0	4.040
97	HME-20	3	LAKEBED	167	7.30	56.700	0.716	98.0	40.500
98	HME-21	3	LAKEBED	168	7.80	33.900	0.000	14.0	20.400
99	LRG-12	3	LAKEBED	127	8.70	5.680	0.000	129.0	3.260
100	HME-23	3	LAKEBED	170	7.50	22.000	0.000	48.0	11.300
101	HME-24	3	LAKEBED	171	7.50	27.800	0.000	61.4	14.700
102	HME-25	3	LAKEBED	172	7.60	24.900	0.000	54.9	13.600
103	LRG-01	3	LAKEBED	116	8.50	6.780	0.513	95.3	4.180
104	LRG-17	3	LAKEBED	91	8.00	11.600	0.296	69.5	7.870
105	LRG-03	3	LAKEBED	118	8.40	8.840	0.663	145.0	4.670
106	LRG-19	3	LAKEBED	93	7.70	27.200	0.454	152.0	16.900
107	LRG-05	3	LAKEBED	120	8.30	10.200	0.454	150.0	5.270
108	LRG-13	3	LAKEBED	128	8.20	97.800	0.078	381.0	67.700
109	LRG-07	3	LAKEBED	122	8.60	22.100	0.723	315.0	12.500
110	LRG-08	3	LAKEBED	123	8.10	11.300	0.409	195.0	6.700
111	LRG-16	3	LAKEBED	131	7.80	14.700	1.350	79.0	7.790
112	LRG-25	3	LAKEBED	99	8.30	12.100	0.000	80.8	6.490
113	LRG-14	3	LAKEBED	129	7.70	31.200	0.000	155.0	18.200
114	LRG-15	3	LAKEBED	130	7.80	16.300	0.813	80.1	8.530
115	LRG-20	3	LAKEBED	94	7.40	39.500	1.250	238.0	24.800
116	LRG-23	3	LAKEBED	97	9.30	70.800	0.000	14.0	58.300

Data file **116PONDS**
Title: CHEMICAL ANALYSES OF POND WATERS OF WESTERN SAN JOAQUIN VALLEY,CA

Function: PRLIST
Data case no. 1 to 30
Without selection

LIST OF VARIABLES

VAR	TYPE	NAME/DESCRIPTION
1	text 12	FIELD NUMBER
2	numeric	GEOLOGICAL ZONE
3	text 8	GEOLOGICAL ZONE
4	numeric	LAB. NUMBER
10	numeric	Ba (mg L^-1)/direct
11	numeric	Ca (mg L^-1)/direct
12	numeric	Cd (mg L^-1)/solvent ext.
13	numeric	Cr (mg L^-1)/solvent ext.
14	numeric	Cu (mg L^-1)/solvent ext.

CASE NO.	1	2	3	4	10	11	12	13	14
1	ALT-01	1	ALLUVIAL	179	0.012	571.000	0.000	0.006	0.007
2	ALT-02	1	ALLUVIAL	180	0.000	494.000	0.000	0.004	0.007
3	ALT-03	1	ALLUVIAL	181	0.000	585.000	0.000	0.001	0.007
4	ALT-04	1	ALLUVIAL	182	0.031	691.000	0.000	0.002	0.009
5	ALT-05	1	ALLUVIAL	183	0.000	588.000	0.000	0.002	0.010
6	ALT-06	1	ALLUVIAL	184	0.025	630.000	0.000	0.000	0.008
7	ALT-07	1	ALLUVIAL	185	0.000	608.000	0.000	0.004	0.007
8	ALT-17	1	ALLKUVIA	84	0.000	683.000	0.001	0.000	0.010
9	ALT-18	1	ALLUVIAL	85	0.022	672.000	0.000	0.000	0.010
10	ALT-19	1	ALLUVIAL	86	0.083	676.000	0.000	0.000	0.013
11	ALT-20	1	ALLUVIAL	87	0.102	545.000	0.000	0.000	0.007
12	HME-18	1	ALLUVIAL	165	0.014	712.000	0.001	0.000	0.006
13	ALT-22	1	ALLUVIAL	89	0.022	753.000	0.001	0.000	0.007
14	ALT-23	1	ALLUVIAL	90	0.030	669.000	0.000	0.000	0.007
15	BJG-04	1	ALLUVIAL	140	0.000	512.000	0.000	0.000	0.014
16	BJG-05	1	ALLUVIAL	141	0.028	537.000	0.000	0.000	0.008
17	BJG-06	1	ALLUVIAL	142	0.000	498.000	0.000	0.003	0.008
18	BJG-07	1	ALLUVIAL	143	0.000	581.000	0.000	0.002	0.008
19	BJG-08	1	ALLUVIAL	144	0.015	734.000	0.000	0.001	0.008
20	BJG-09	1	ALLUVIAL	145	0.000	641.000	0.000	0.000	0.006
21	BJG-10	1	ALLUVIAL	146	0.000	524.000	0.000	0.008	0.005
22	BJG-11	1	ALLUVIAL	147	0.005	517.000	0.000	0.013	0.004
23	HME-14	1	ALLUVIAL	81	0.018	734.000	0.000	0.000	0.005
24	HME-15	1	ALLUVIAL	82	0.000	571.000	0.000	0.004	0.006
25	HME-16	1	ALLUVIAL	83	0.008	702.000	0.000	0.000	0.005
26	HME-17	1	ALLUVIAL	164	0.001	826.000	0.000	0.000	0.003
27	EWJ-06	2	BASINRIM	105	0.008	428.000	0.000	0.000	0.003
28	BJG-01	2	BASINRIM	137	0.054	544.000	0.000	0.000	0.012
29	BJG-02	2	BASINRIM	138	0.000	531.000	0.000	0.005	0.010
30	EWJ-08	2	BASINRIM	107	0.011	462.000	0.000	0.008	0.006

Data file 116PONDS
Title: CHEMICAL ANALYSES OF POND WATERS OF WESTERN SAN JOAQUIN VALLEY,CA

Function: PRLIST
Data case no. 31 to 60
Without selection

LIST OF VARIABLES

VAR	TYPE	NAME/DESCRIPTION
1	text 12	FIELD NUMBER
2	numeric	GEOLOGICAL ZONE
3	text 8	GEOLOGICAL ZONE
4	numeric	LAB. NUMBER
10	numeric	Ba (mg L^{-1})/direct
11	numeric	Ca (mg L^{-1})/direct
12	numeric	Cd (mg L^{-1})/solvent ext.
13	numeric	Cr (mg L^{-1})/solvent ext.
14	numeric	Cu (mg L^{-1})/solvent ext.

CASE NO.	1	2	3	4	10	11	12	13	14
31	BY-01	2	BASINRIM	148	0.038	389.000	0.000	0.000	0.009
32	BY-02	2	BASINRIM	149	0.022	732.000	0.000	0.000	0.004
33	BY-03	2	BASINRIM	150	0.053	569.000	0.000	0.000	0.004
34	BY-04	2	BASINRIM	151	0.000	432.000	0.000	0.000	0.004
35	BY-05	2	BASINRIM	152	0.000	480.000	0.000	0.000	0.002
36	BY-06	2	BASINRIM	153	0.000	468.000	0.000	0.000	0.004
37	BY-07	2	BASINRIM	154	0.000	506.000	0.000	0.000	0.003
38	EWJ-01	2	BASINRIM	100	0.039	638.000	0.000	0.000	0.003
39	EWJ-02	2	BASINRIM	101	0.000	605.000	0.000	0.000	0.003
40	EWJ-03	2	BASINRIM	102	0.000	466.000	0.000	0.000	0.001
41	EWJ-04	2	BASINRIM	103	0.000	416.000	0.000	0.000	0.006
42	EWJ-05	2	BASINRIM	104	0.000	326.000	0.000	0.000	0.002
43	EWJ-21	2	BASINRIM	136	0.000	205.000	0.000	0.000	0.002
44	EWJ-07	2	BASINRIM	106	0.040	653.000	0.000	0.000	0.005
45	EWJ-15	2	BASINRIM	114	0.013	134.000	0.000	0.000	0.005
46	EWJ-09	2	BASINRIM	108	0.025	568.000	0.000	0.000	0.004
47	EWJ-10	2	BASINRIM	109	0.000	418.000	0.000	0.001	0.005
48	EWJ-11	2	BASINRIM	110	0.000	153.000	0.000	0.000	0.004
49	EWJ-19	2	BASINRIM	134	0.000	144.000	0.000	0.000	0.008
50	EWJ-13	2	BASINRIM	112	0.000	135.000	0.000	0.000	0.003
51	EWJ-14	2	BASINRIM	113	0.007	94.200	0.000	0.000	0.010
52	EWJ-18	2	BASAINRI	133	0.000	148.000	0.000	0.000	0.010
53	EWJ-16	2	BASINRIM	115	0.028	215.000	0.000	0.000	0.010
54	EWJ-17	2	BASINRIM	132	0.017	209.000	0.000	0.000	0.006
55	HME-11	3	LAKEBED	78	0.000	310.000	0.000	0.000	0.009
56	LRG-10	3	LAKEBED	125	0.000	42.400	0.000	0.000	0.012
57	LRG-18	3	LAKEBED	92	0.000	53.000	0.000	0.000	0.011
58	BY-15	3	LAKEBED	162	0.000	95.900	0.000	0.000	0.003
59	ALT-08	3	LAKEBED	186	0.000	125.000	0.000	0.000	0.004
60	ALT-09	3	LAKEBED	187	0.000	67.600	0.000	0.000	0.001

Data file 116PONDS
Title: CHEMICAL ANALYSES OF POND WATERS OF WESTERN SAN JOAQUIN VALLEY,CA

Function: PRLIST
Data case no. 61 to 90
Without selection

LIST OF VARIABLES

VAR	TYPE	NAME/DESCRIPTION
1	text 12	FIELD NUMBER
2	numeric	GEOLOGICAL ZONE
3	text 8	GEOLOGICAL ZONE
4	numeric	LAB. NUMBER
10	numeric	Ba (mg L^-1)/direct
11	numeric	Ca (mg L^-1)/direct
12	numeric	Cd (mg L^-1)/solvent ext.
13	numeric	Cr (mg L^-1)/solvent ext.
14	numeric	Cu (mg L^-1)/solvent ext.

CASE NO.	1	2	3	4	10	11	12	13	14
61	HME-10	3	LAKEBED	77	0.022	376.000	0.000	0.000	0.002
62	ALT-11	3	LAKEBED	189	0.012	279.000	0.000	0.000	0.005
63	ALT-12	3	LAKEBED	190	0.000	71.800	0.000	0.000	0.003
64	ALT-13	3	LAKEBED	191	0.023	122.000	0.000	0.000	0.005
65	ALT-14	3	LAKEBED	192	0.004	167.000	0.000	0.000	0.003
66	ALT-15	3	LAKEBED	193	0.012	152.000	0.000	0.000	0.003
67	ALT-16	3	LAKEBED	194	0.023	160.000	0.000	0.000	0.002
68	By-08	3	LAKEBED	155	0.013	144.000	0.000	0.001	0.001
69	BY-09	3	LAKEBED	156	0.006	100.000	0.000	0.000	0.001
70	BY-10	3	LAKEBED	157	0.000	83.900	0.000	0.000	0.002
71	BY-11	3	LAKEBED	158	0.003	89.200	0.000	0.000	0.004
72	BY-12	3	LAKEBED	159	0.000	84.400	0.000	0.000	0.004
73	LRG-02	3	LAKEBED	117	0.000	10.600	0.000	0.000	0.009
74	BY-14	3	LAKEBED	161	0.000	82.400	0.000	0.000	0.002
75	LRG-04	3	LAKEBED	119	0.000	20.700	0.000	0.000	0.007
76	BY-16	3	LAKEBED	163	0.005	87.900	0.000	0.000	0.003
77	BY-17	3	LAKEBED	173	0.000	66.300	0.000	0.000	0.002
78	BY-18	3	LAKEBED	174	0.000	97.900	0.000	0.000	0.005
79	BY-19	3	LAKEBED	175	0.000	73.000	0.000	0.000	0.006
80	BY-20	3	LAKEBED	176	0.023	178.000	0.000	0.001	0.002
81	HME-19	3	LAKEBED	166	0.025	759.000	0.000	0.000	0.004
82	BY-22	3	LAKEBED	178	0.000	282.000	0.000	0.000	0.001
83	HME-01	3	LAKEBED	68	0.021	323.000	0.000	0.000	0.005
84	HME-02	3	LAKEBED	69	0.000	194.000	0.000	0.000	0.003
85	HME-03	3	LAKEBED	70	0.000	244.000	0.000	0.000	0.006
86	HME-04	3	LAKEBED	71	0.000	186.000	0.000	0.000	0.004
87	HME-05	3	LAKEBED	72	0.020	581.000	0.000	0.000	0.007
88	HME-06	3	LAKEBED	73	0.042	911.000	0.000	0.000	0.001
89	HME-07	3	LAKEBED	74	0.022	633.000	0.000	0.000	0.002
90	HME-08	3	LAKEBED	75	0.000	632.000	0.000	0.000	0.003

Data file 116PONDS
Title: CHEMICAL ANALYSES OF POND WATERS OF WESTERN SAN JOAQUIN VALLEY,CA

Function: PRLIST
Data case no. 91 to 116
Without selection

LIST OF VARIABLES

VAR   TYPE   NAME/DESCRIPTION
  1   text 12   FIELD NUMBER
  2   numeric   GEOLOGICAL ZONE
  3   text 8   GEOLOGICAL ZONE
  4   numeric   LAB. NUMBER
 10   numeric   Ba (mg L^-1)/direct
 11   numeric   Ca (mg L^-1)/direct
 12   numeric   Cd (mg L^-1)/solvent ext.
 13   numeric   Cr (mg L^-1)/solvent ext.
 14   numeric   Cu (mg L^-1)/solvent ext.

CASE
NO.   1   2   3   4   10   11   12   13   14
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   91   HME-09   3 LAKEBED   76   0.000   307.000   0.000   0.000   0.007
   92   LRG-21   3 LAKEBED   95   0.009   80.200   0.000   0.000   0.001
   93   LRG-06   3 LAKEBED   121   0.005   7.780   0.000   0.001   0.005
   94   HME-12   3 LAKEBED   79   0.000   8.900   0.000   0.000   0.009
   95   LRG-24   3 LAKEBED   98   0.025   146.000   0.000   0.000   0.005
   96   LRG-09   3 LAKEBED   124   0.000   32.200   0.000   0.000   0.006
   97   HME-20   3 LAKEBED   167   0.032   637.000   0.000   0.000   0.001
   98   HME-21   3 LAKEBED   168   0.000   626.000   0.000   0.000   0.007
   99   LRG-12   3 LAKEBED   127   0.000   47.400   0.000   0.000   0.010
  100   HME-23   3 LAKEBED   170   0.000   518.000   0.000   0.000   0.005
  101   HME-24   3 LAKEBED   171   0.000   517.000   0.000   0.000   0.003
  102   HME-25   3 LAKEBED   172   0.000   531.000   0.000   0.000   0.004
  103   LRG-01   3 LAKEBED   116   0.020   86.000   0.000   0.000   0.012
  104   LRG-17   3 LAKEBED   91   0.000   59.700   0.000   0.000   0.005
  105   LRG-03   3 LAKEBED   118   0.000   17.700   0.000   0.000   0.005
  106   LRG-19   3 LAKEBED   93   0.000   46.700   0.000   0.000   0.001
  107   LRG-05   3 LAKEBED   120   0.000   14.700   0.000   0.000   0.007
  108   LRG-13   3 LAKEBED   128   0.004   190.000   0.000   0.000   0.005
  109   LRG-07   3 LAKEBED   122   0.000   25.300   0.000   0.001   0.004
  110   LRG-08   3 LAKEBED   123   0.000   18.900   0.000   0.000   0.005
  111   LRG-16   3 LAKEBED   131   0.024   36.600   0.000   0.000   0.009
  112   LRG-25   3 LAKEBED   99   0.000   144.000   0.000   0.000   0.011
  113   LRG-14   3 LAKEBED   129   0.000   85.600   0.000   0.000   0.002
  114   LRG-15   3 LAKEBED   130   0.000   39.600   0.000   0.000   0.003
  115   LRG-20   3 LAKEBED   94   0.014   61.200   0.000   0.000   0.002
  116   LRG-23   3 LAKEBED   97   0.006   198.000   0.000   0.000   0.006

Data file **116PONDS**
Title: CHEMICAL ANALYSES OF POND WATERS OF WESTERN SAN JOAQUIN VALLEY,CA

Function: PRLIST
Data case no. 1 to 30
Without selection

LIST OF VARIABLES

VAR	TYPE	NAME/DESCRIPTION
1	text 12	FIELD NUMBER
2	numeric	GEOLOGICAL ZONE
3	text 8	GEOLOGICAL ZONE
4	numeric	LAB. NUMBER
15	numeric	Fe (mg L^{-1})/solvent ext.
16	numeric	K (mg L^{-1})/direct
17	numeric	Li (mg L^{-1})/direct
18	numeric	Mg (mg L^{-1})/direct
19	numeric	Mn (mg L^{-1})/solvent ext.

CASE NO.	1	2	3	4	15	16	17	18	19
1	ALT-01	1	ALLUVIAL	179	0.012	27.90	0.156	773.00	0.005
2	ALT-02	1	ALLUVIAL	180	0.008	25.80	0.082	744.00	0.006
3	ALT-03	1	ALLUVIAL	181	0.009	45.20	0.232	947.00	0.006
4	ALT-04	1	ALLUVIAL	182	0.016	199.00	1.660	4410.00	0.016
5	ALT-05	1	ALLUVIAL	183	0.011	36.60	0.228	1000.00	0.005
6	ALT-06	1	ALLUVIAL	184	0.027	82.00	0.545	1680.00	0.005
7	ALT-07	1	ALLUVIAL	185	0.015	31.70	0.105	908.00	0.007
8	ALT-17	1	ALLKUVIA	84	0.018	21.10	0.578	968.00	0.025
9	ALT-18	1	ALLUVIAL	85	0.020	23.30	0.778	952.00	0.011
10	ALT-19	1	ALLUVIAL	86	0.005	31.20	1.110	1530.00	0.002
11	ALT-20	1	ALLUVIAL	87	0.006	43.10	1.420	1280.00	0.001
12	HME-18	1	ALLUVIAL	165	0.010	19.90	0.683	942.00	0.000
13	ALT-22	1	ALLUVIAL	89	0.015	17.80	0.495	722.00	0.006
14	ALT-23	1	ALLUVIAL	90	0.010	17.10	0.562	625.00	0.007
15	BJG-04	1	ALLUVIAL	140	0.007	55.70	1.700	867.00	0.004
16	BJG-05	1	ALLUVIAL	141	0.012	35.60	0.917	587.00	0.007
17	BJG-06	1	ALLUVIAL	142	0.008	12.50	0.090	145.00	0.006
18	BJG-07	1	ALLUVIAL	143	0.026	15.00	0.211	188.00	0.015
19	BJG-08	1	ALLUVIAL	144	0.025	21.10	0.311	287.00	0.006
20	BJG-09	1	ALLUVIAL	145	0.008	24.50	0.510	351.00	0.006
21	BJG-10	1	ALLUVIAL	146	0.006	9.71	0.000	465.00	0.008
22	BJG-11	1	ALLUVIAL	147	0.022	9.79	0.010	495.00	0.014
23	HME-14	1	ALLUVIAL	81	0.041	13.30	0.590	428.00	0.007
24	HME-15	1	ALLUVIAL	82	0.003	6.07	0.150	223.00	0.003
25	HME-16	1	ALLUVIAL	83	0.009	9.62	0.563	467.00	0.006
26	HME-17	1	ALLUVIAL	164	0.005	13.60	0.341	578.00	0.006
27	EWJ-06	2	BASINRIM	105	0.032	7.85	0.000	916.00	0.037
28	BJG-01	2	BASINRIM	137	0.038	58.30	1.150	8920.00	0.479
29	BJG-02	2	BASINRIM	138	0.007	10.40	0.240	2310.00	0.013
30	EWJ-08	2	BASINRIM	107	0.012	5.88	0.000	527.00	0.008

Data file 116PONDS
Title: CHEMICAL ANALYSES OF POND WATERS OF WESTERN SAN JOAQUIN VALLEY,CA

Function: PRLIST
Data case no. 31 to 60
Without selection

LIST OF VARIABLES

VAR   TYPE   NAME/DESCRIPTION
  1   text 12   FIELD NUMBER
  2   numeric   GEOLOGICAL ZONE
  3   text 8   GEOLOGICAL ZONE
  4   numeric   LAB. NUMBER
 15   numeric   Fe (mg L^-1)/solvent ext.
 16   numeric   K (mg L^-1)/direct
 17   numeric   Li (mg L^-1)/direct
 18   numeric   Mg (mg L^-1)/direct
 19   numeric   Mn (mg L^-1)/solvent ext.

CASE
NO.   1 2   3   4   15   16   17   18   19
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 31   BY-01   2 BASINRIM 148   0.045   10.10   0.000   733.00   0.685
 32   BY-02   2 BASINRIM 149   0.024   21.90   0.092   2850.00   0.274
 33   BY-03   2 BASINRIM 150   0.016   27.70   0.188   2810.00   0.107
 34   BY-04   2 BASINRIM 151   0.007   13.30   0.000   836.00   0.051
 35   BY-05   2 BASINRIM 152   0.007   17.10   0.000   1360.00   0.007
 36   BY-06   2 BASINRIM 153   0.018   18.10   0.000   1300.00   0.091
 37   BY-07   2 BASINRIM 154   0.018   17.80   0.000   1440.00   0.007
 38   EWJ-01   2 BASINRIM 100   0.062   15.30   0.078   2630.00   0.283
 39   EWJ-02   2 BASINRIM 101   0.141   18.40   0.000   2620.00   0.506
 40   EWJ-03   2 BASINRIM 102   0.032   10.50   0.000   989.00   0.094
 41   EWJ-04   2 BASINRIM 103   0.028   8.93   0.000   753.00   0.267
 42   EWJ-05   2 BASINRIM 104   0.144   5.07   0.000   424.00   0.083
 43   EWJ-21   2 BASINRIM 136   0.007   15.50   0.000   649.00   0.004
 44   EWJ-07   2 BASINRIM 106   0.033   35.40   0.272   5310.00   0.089
 45   EWJ-15   2 BASINRIM 114   0.011   13.10   0.000   428.00   0.008
 46   EWJ-09   2 BASINRIM 108   0.013   42.90   0.239   4750.00   0.059
 47   EWJ-10   2 BASINRIM 109   0.102   9.33   0.000   554.00   0.133
 48   EWJ-11   2 BASINRIM 110   0.012   17.80   0.000   604.00   0.001
 49   EWJ-19   2 BASINRIM 134   0.015   12.50   0.000   455.00   0.012
 50   EWJ-13   2 BASINRIM 112   0.011   17.60   0.000   655.00   0.010
 51   EWJ-14   2 BASINRIM 113   0.008   8.61   0.000   184.00   0.009
 52   EWJ-18   2 BASAINRI 133   0.017   12.80   0.000   406.00   0.007
 53   EWJ-16   2 BASINRIM 115   0.008   7.40   0.000   446.00   0.007
 54   EWJ-17   2 BASINRIM 132   0.004   10.70   0.000   282.00   0.004
 55   HME-11   3 LAKEBED   78   0.009   20.50   0.000   356.00   0.000
 56   LRG-10   3 LAKEBED   125   0.020   3.14   0.000   51.60   0.008
 57   LRG-18   3 LAKEBED   92   0.012   19.10   0.000   343.00   0.007
 58   BY-15   3 LAKEBED   162   0.024   22.50   0.094   496.00   0.011
 59   ALT-08   3 LAKEBED   186   0.016   5.96   0.255   135.00   0.013
 60   ALT-09   3 LAKEBED   187   0.009   6.06   0.393   167.00   0.006

LIST OF VARIABLES

VAR	TYPE	NAME/DESCRIPTION
1	text 12	FIELD NUMBER
2	numeric	GEOLOGICAL ZONE
3	text 8	GEOLOGICAL ZONE
4	numeric	LAB. NUMBER
15	numeric	Fe (mg L^-1)/solvent ext.
16	numeric	K (mg L^-1)/direct
17	numeric	Li (mg L^-1)/direct
18	numeric	Mg (mg L^-1)/direct
19	numeric	Mn (mg L^-1)/solvent ext.

CASE NO.	1	2	3	4	15	16	17	18	19
61	HME-10	3	LAKEBED	77	0.017	32.10	0.273	611.00	0.005
62	ALT-11	3	LAKEBED	189	0.038	151.00	4.100	1370.00	0.002
63	ALT-12	3	LAKEBED	190	0.016	32.50	0.525	168.00	0.010
64	ALT-13	3	LAKEBED	191	0.016	84.80	1.210	384.00	0.021
65	ALT-14	3	LAKEBED	192	0.018	18.20	0.252	105.00	0.010
66	ALT-15	3	LAKEBED	193	0.019	15.30	0.295	100.00	0.009
67	ALT-16	3	LAKEBED	194	0.016	23.20	0.420	157.00	0.006
68	By-08	3	LAKEBED	155	0.029	61.90	0.496	1330.00	0.030
69	BY-09	3	LAKEBED	156	0.033	42.80	0.187	828.00	0.008
70	BY-10	3	LAKEBED	157	0.009	45.60	0.282	874.00	0.005
71	BY-11	3	LAKEBED	158	0.052	69.00	0.532	1490.00	0.013
72	BY-12	3	LAKEBED	159	0.051	52.30	0.172	1030.00	0.014
73	LRG-02	3	LAKEBED	117	0.025	7.17	0.000	108.00	0.009
74	BY-14	3	LAKEBED	161	0.023	37.90	0.269	725.00	0.010
75	LRG-04	3	LAKEBED	119	0.029	5.23	0.000	81.30	0.012
76	BY-16	3	LAKEBED	163	0.009	22.10	0.081	474.00	0.008
77	BY-17	3	LAKEBED	173	0.023	40.20	0.236	668.00	0.013
78	BY-18	3	LAKEBED	174	0.013	17.10	0.000	310.00	0.008
79	BY-19	3	LAKEBED	175	0.009	17.80	0.010	350.00	0.006
80	BY-20	3	LAKEBED	176	0.032	197.00	1.640	3420.00	0.004
81	HME-19	3	LAKEBED	166	0.009	230.00	1.340	4490.00	0.121
82	BY-22	3	LAKEBED	178	0.007	27.50	0.348	547.00	0.008
83	HME-01	3	LAKEBED	68	0.022	50.10	0.389	1980.00	0.187
84	HME-02	3	LAKEBED	69	0.045	30.80	0.127	1210.00	0.793
85	HME-03	3	LAKEBED	70	0.009	22.40	0.052	584.00	0.231
86	HME-04	3	LAKEBED	71	0.028	32.90	0.097	1180.00	0.551
87	HME-05	3	LAKEBED	72	0.005	33.30	0.241	1410.00	0.000
88	HME-06	3	LAKEBED	73	0.010	33.50	0.402	1570.00	0.000
89	HME-07	3	LAKEBED	74	0.015	55.60	0.602	2170.00	0.000
90	HME-08	3	LAKEBED	75	0.008	48.90	0.305	914.00	0.006

Data file **116PONDS**
Title: CHEMICAL ANALYSES OF POND WATERS OF WESTERN SAN JOAQUIN VALLEY,CA

Function: PRLIST
Data case no. 91 to 116
Without selection

LIST OF VARIABLES

VAR	TYPE	NAME/DESCRIPTION
1	text 12	FIELD NUMBER
2	numeric	GEOLOGICAL ZONE
3	text 8	GEOLOGICAL ZONE
4	numeric	LAB. NUMBER
15	numeric	Fe (mg L^-1)/solvent ext.
16	numeric	K (mg L^-1)/direct
17	numeric	Li (mg L^-1)/direct
18	numeric	Mg (mg L^-1)/direct
19	numeric	Mn (mg L^-1)/solvent ext.

CASE NO.	1	2	3	4	15	16	17	18	19
91	HME-09	3	LAKEBED	76	0.012	24.70	0.042	415.00	0.007
92	LRG-21	3	LAKEBED	95	0.024	101.00	0.707	1830.00	0.001
93	LRG-06	3	LAKEBED	121	0.021	10.60	0.000	152.00	0.010
94	HME-12	3	LAKEBED	79	0.027	109.00	0.321	335.00	0.000
95	LRG-24	3	LAKEBED	98	0.017	70.50	0.502	1640.00	0.004
96	LRG-09	3	LAKEBED	124	0.013	3.89	0.000	72.40	0.007
97	HME-20	3	LAKEBED	167	0.014	154.00	0.846	2940.00	0.024
98	HME-21	3	LAKEBED	168	0.010	69.60	0.276	1340.00	0.011
99	LRG-12	3	LAKEBED	127	0.009	3.31	0.000	69.20	0.009
100	HME-23	3	LAKEBED	170	0.006	55.40	0.220	963.00	0.009
101	HME-24	3	LAKEBED	171	0.010	85.00	0.376	1200.00	0.012
102	HME-25	3	LAKEBED	172	0.026	65.40	0.214	1280.00	0.053
103	LRG-01	3	LAKEBED	116	0.045	6.31	0.000	121.00	0.067
104	LRG-17	3	LAKEBED	91	0.022	19.80	0.000	233.00	0.011
105	LRG-03	3	LAKEBED	118	0.025	6.90	0.000	123.00	0.010
106	LRG-19	3	LAKEBED	93	0.011	31.10	0.115	627.00	0.007
107	LRG-05	3	LAKEBED	120	0.031	7.64	0.000	141.00	0.009
108	LRG-13	3	LAKEBED	128	0.056	134.00	1.260	2430.00	0.064
109	LRG-07	3	LAKEBED	122	0.011	18.90	0.000	252.00	0.008
110	LRG-08	3	LAKEBED	123	0.009	10.30	0.000	148.00	0.009
111	LRG-16	3	LAKEBED	131	0.014	19.80	0.032	288.00	0.012
112	LRG-25	3	LAKEBED	99	0.011	15.00	0.000	21.00	0.008
113	LRG-14	3	LAKEBED	129	0.009	42.10	0.144	696.00	0.006
114	LRG-15	3	LAKEBED	130	0.008	24.00	0.044	320.00	0.005
115	LRG-20	3	LAKEBED	94	0.019	46.80	0.256	931.00	0.008
116	LRG-23	3	LAKEBED	97	0.018	93.80	0.673	2060.00	0.004

Data file 116PONDS
Title: CHEMICAL ANALYSES OF POND WATERS OF WESTERN SAN JOAQUIN VALLEY,CA

Function: PRLIST
Data case no. 1 to 30
Without selection

LIST OF VARIABLES

VAR	TYPE	NAME/DESCRIPTION
1	text 12	FIELD NUMBER
2	numeric	GEOLOGICAL ZONE
3	text 8	GEOLOGICAL ZONE
4	numeric	LAB. NUMBER
20	numeric	Mo (mg L^{-1})/direct
21	numeric	Na (mg L^{-1})/direct
22	numeric	Ni (mg L^{-1})/solvent ext.
23	numeric	P (mg L^{-1})/direct
24	numeric	Pb (mg L^{-1})/solvent ext.

CASE NO.	1	2	3	4	20	21	22	23	24
1	ALT-01	1	ALLUVIAL	179	2.070	8850.0	0.002	0.234	0.000
2	ALT-02	1	ALLUVIAL	180	2.200	8600.0	0.003	0.000	0.000
3	ALT-03	1	ALLUVIAL	181	2.620	11100.0	0.004	0.000	0.000
4	ALT-04	1	ALLUVIAL	182	12.700	55600.0	0.004	0.000	0.000
5	ALT-05	1	ALLUVIAL	183	2.740	11600.0	0.004	0.000	0.000
6	ALT-06	1	ALLUVIAL	184	4.410	20600.0	0.002	0.000	0.000
7	ALT-07	1	ALLUVIAL	185	2.410	10600.0	0.004	0.000	0.000
8	ALT-17	1	ALLKUVIA	84	2.280	26400.0	0.007	0.000	0.000
9	ALT-18	1	ALLUVIAL	85	2.340	26100.0	0.006	0.198	0.000
10	ALT-19	1	ALLUVIAL	86	3.660	41100.0	0.006	0.004	0.035
11	ALT-20	1	ALLUVIAL	87	4.230	34400.0	0.006	0.000	0.010
12	HME-18	1	ALLUVIAL	165	2.160	26600.0	0.006	0.000	0.000
13	ALT-22	1	ALLUVIAL	89	1.570	20600.0	0.003	0.401	0.000
14	ALT-23	1	ALLUVIAL	90	1.520	16300.0	0.006	0.434	0.000
15	BJG-04	1	ALLUVIAL	140	0.488	16200.0	0.012	0.000	0.004
16	BJG-05	1	ALLUVIAL	141	0.184	11500.0	0.010	0.000	0.000
17	BJG-06	1	ALLUVIAL	142	0.061	2290.0	0.006	0.000	0.003
18	BJG-07	1	ALLUVIAL	143	0.110	3670.0	0.008	0.137	0.000
19	BJG-08	1	ALLUVIAL	144	0.134	5620.0	0.007	0.000	0.000
20	BJG-09	1	ALLUVIAL	145	0.122	7190.0	0.007	0.133	0.000
21	BJG-10	1	ALLUVIAL	146	0.170	5940.0	0.005	0.000	0.000
22	BJG-11	1	ALLUVIAL	147	0.246	6340.0	0.006	0.246	0.000
23	HME-14	1	ALLUVIAL	81	1.600	10400.0	0.005	0.198	0.000
24	HME-15	1	ALLUVIAL	82	0.859	5150.0	0.001	0.000	0.000
25	HME-16	1	ALLUVIAL	83	1.610	11600.0	0.004	0.275	0.000
26	HME-17	1	ALLUVIAL	164	1.280	15100.0	0.004	0.000	0.000
27	EWJ-06	2	BASINRIM	105	0.385	6710.0	0.004	0.002	0.000
28	BJG-01	2	BASINRIM	137	1.510	51400.0	0.016	2.350	0.003
29	BJG-02	2	BASINRIM	138	0.455	15400.0	0.008	0.000	0.004
30	EWJ-08	2	BASINRIM	107	0.833	6730.0	0.003	0.166	0.000

Data file 116PONDS
Title: CHEMICAL ANALYSES OF POND WATERS OF WESTERN SAN JOAQUIN VALLEY,CA

Function: PRLIST
Data case no. 31 to 60
Without selection

LIST OF VARIABLES

VAR   TYPE   NAME/DESCRIPTION
  1   text 12   FIELD NUMBER
  2   numeric   GEOLOGICAL ZONE
  3   text 8   GEOLOGICAL ZONE
  4   numeric   LAB. NUMBER
 20   numeric   Mo (mg L^-1)/direct
 21   numeric   Na (mg L^-1)/direct
 22   numeric   Ni (mg L^-1)/solvent ext.
 23   numeric   P (mg L^-1)/direct
 24   numeric   Pb (mg L^-1)/solvent ext.

CASE
NO.   1 2   3   4   20   21   22   23   24

31	BY-01	2	BASINRIM	148	0.236	7950.0	0.006	1.220	0.000
32	BY-02	2	BASINRIM	149	1.480	35000.0	0.012	0.935	0.000
33	BY-03	2	BASINRIM	150	2.210	34400.0	0.012	1.440	0.000
34	BY-04	2	BASINRIM	151	0.176	8870.0	0.004	0.517	0.000
35	BY-05	2	BASINRIM	152	0.384	15100.0	0.005	0.734	0.000
36	BY-06	2	BASINRIM	153	0.424	14500.0	0.007	0.592	0.000
37	BY-07	2	BASINRIM	154	0.365	16100.0	0.007	0.196	0.000
38	EWJ-01	2	BASINRIM	100	0.693	25100.0	0.003	0.292	0.000
39	EWJ-02	2	BASINRIM	101	0.712	25300.0	0.006	0.016	0.000
40	EWJ-03	2	BASINRIM	102	0.272	7190.0	0.002	0.000	0.000
41	EWJ-04	2	BASINRIM	103	0.267	6110.0	0.007	0.171	0.004
42	EWJ-05	2	BASINRIM	104	0.117	2550.0	0.002	0.000	0.000
43	EWJ-21	2	BASINRIM	136	0.456	6470.0	0.001	0.208	0.004
44	EWJ-07	2	BASINRIM	106	0.952	48900.0	0.006	0.107	0.000
45	EWJ-15	2	BASINRIM	114	0.498	7140.0	0.004	0.717	0.007
46	EWJ-09	2	BASINRIM	108	1.010	42900.0	0.006	0.000	0.000
47	EWJ-10	2	BASINRIM	109	0.804	6660.0	0.003	0.000	0.000
48	EWJ-11	2	BASINRIM	110	0.768	8950.0	0.003	0.158	0.000
49	EWJ-19	2	BASINRIM	134	0.281	4420.0	0.005	0.000	0.005
50	EWJ-13	2	BASINRIM	112	0.891	10500.0	0.005	0.000	0.000
51	EWJ-14	2	BASINRIM	113	0.278	3410.0	0.004	0.500	0.006
52	EWJ-18	2	BASAINRI	133	0.227	3890.0	0.005	0.020	0.005
53	EWJ-16	2	BASINRIM	115	0.694	5580.0	0.005	0.492	0.003
54	EWJ-17	2	BASINRIM	132	0.216	2360.0	0.001	0.428	0.003
55	HME-11	3	LAKEBED	78	2.830	5800.0	0.002	0.000	0.000
56	LRG-10	3	LAKEBED	125	0.138	1590.0	0.004	1.110	0.004
57	LRG-18	3	LAKEBED	92	1.110	4590.0	0.005	0.000	0.004
58	BY-15	3	LAKEBED	162	1.790	8390.0	0.004	0.088	0.000
59	ALT-08	3	LAKEBED	186	2.670	7170.0	0.003	0.073	0.000
60	ALT-09	3	LAKEBED	187	4.870	10600.0	0.001	0.038	0.000

Data file 116PONDS
Title: CHEMICAL ANALYSES OF POND WATERS OF WESTERN SAN JOAQUIN VALLEY,CA

Function: PRLIST
Data case no. 61 to 90
Without selection

LIST OF VARIABLES

VAR	TYPE	NAME/DESCRIPTION
1	text 12	FIELD NUMBER
2	numeric	GEOLOGICAL ZONE
3	text 8	GEOLOGICAL ZONE
4	numeric	LAB. NUMBER
20	numeric	Mo (mg L^-1)/direct
21	numeric	Na (mg L^-1)/direct
22	numeric	Ni (mg L^-1)/solvent ext.
23	numeric	P (mg L^-1)/direct
24	numeric	Pb (mg L^-1)/solvent ext.

CASE NO.	1	2	3	4	20	21	22	23	24
61	HME-10	3	LAKEBED	77	4.660	11600.0	0.001	0.401	0.000
62	ALT-11	3	LAKEBED	189	23.700	76100.0	0.009	0.210	0.100
63	ALT-12	3	LAKEBED	190	6.040	21300.0	0.001	0.000	0.048
64	ALT-13	3	LAKEBED	191	11.500	50200.0	0.002	0.380	0.000
65	ALT-14	3	LAKEBED	192	3.180	5640.0	0.002	0.000	0.000
66	ALT-15	3	LAKEBED	193	3.290	5470.0	0.002	0.148	0.000
67	ALT-16	3	LAKEBED	194	5.290	9190.0	0.003	0.256	0.000
68	By-08	3	LAKEBED	155	3.470	21600.0	0.003	0.330	0.000
69	BY-09	3	LAKEBED	156	2.280	13300.0	0.004	0.309	0.000
70	BY-10	3	LAKEBED	157	2.400	14300.0	0.003	0.027	0.000
71	BY-11	3	LAKEBED	158	3.520	25100.0	0.004	0.351	0.000
72	BY-12	3	LAKEBED	159	2.820	17500.0	0.007	0.000	0.000
73	LRG-02	3	LAKEBED	117	0.230	2630.0	0.006	0.632	0.000
74	BY-14	3	LAKEBED	161	2.260	12200.0	0.004	0.462	0.000
75	LRG-04	3	LAKEBED	119	0.173	1980.0	0.005	1.000	0.000
76	BY-16	3	LAKEBED	163	1.470	8110.0	0.004	0.479	0.000
77	BY-17	3	LAKEBED	173	2.000	11300.0	0.004	0.502	0.000
78	BY-18	3	LAKEBED	174	1.220	4970.0	0.004	0.162	0.000
79	BY-19	3	LAKEBED	175	1.370	5680.0	0.003	0.320	0.000
80	BY-20	3	LAKEBED	176	8.050	54400.0	0.002	0.079	0.007
81	HME-19	3	LAKEBED	166	0.704	35600.0	0.015	0.546	0.000
82	BY-22	3	LAKEBED	178	2.460	11300.0	0.002	0.000	0.000
83	HME-01	3	LAKEBED	68	4.310	33600.0	0.009	0.514	0.004
84	HME-02	3	LAKEBED	69	2.850	18200.0	0.009	0.366	0.000
85	HME-03	3	LAKEBED	70	1.970	8750.0	0.003	0.635	0.000
86	HME-04	3	LAKEBED	71	2.790	17800.0	0.005	0.276	0.000
87	HME-05	3	LAKEBED	72	3.060	17200.0	0.003	0.623	0.000
88	HME-06	3	LAKEBED	73	4.510	18100.0	0.001	0.391	0.000
89	HME-07	3	LAKEBED	74	7.060	25500.0	0.000	0.034	0.000
90	HME-08	3	LAKEBED	75	3.840	13700.0	0.002	0.119	0.000

Data file 116PONDS
Title: CHEMICAL ANALYSES OF POND WATERS OF WESTERN SAN JOAQUIN VALLEY,CA

Function: PRLIST
Data case no. 91 to 116
Without selection

LIST OF VARIABLES

VAR	TYPE	NAME/DESCRIPTION
1	text 12	FIELD NUMBER
2	numeric	GEOLOGICAL ZONE
3	text 8	GEOLOGICAL ZONE
4	numeric	LAB. NUMBER
20	numeric	Mo (mg L^{-1})/direct
21	numeric	Na (mg L^{-1})/direct
22	numeric	Ni (mg L^{-1})/solvent ext.
23	numeric	P (mg L^{-1})/direct
24	numeric	Pb (mg L^{-1})/solvent ext.

CASE NO.	1	2	3	4	20	21	22	23	24
91	HME-09	3	LAKEBED	76	2.440	6330.0	0.004	0.000	0.000
92	LRG-21	3	LAKEBED	95	3.520	28400.0	0.002	0.307	0.000
93	LRG-06	3	LAKEBED	121	0.479	4140.0	0.007	0.600	0.003
94	HME-12	3	LAKEBED	79	4.650	21900.0	0.009	0.564	0.010
95	LRG-24	3	LAKEBED	98	3.530	21500.0	0.005	0.316	0.000
96	LRG-09	3	LAKEBED	124	0.143	1960.0	0.004	0.857	0.000
97	HME-20	3	LAKEBED	167	0.603	20800.0	0.009	0.535	0.000
98	HME-21	3	LAKEBED	168	0.508	10200.0	0.011	0.000	0.000
99	LRG-12	3	LAKEBED	127	0.175	1910.0	0.004	1.040	0.000
100	HME-23	3	LAKEBED	170	0.462	5620.0	0.009	0.000	0.000
101	HME-24	3	LAKEBED	171	0.472	7020.0	0.009	0.363	0.000
102	HME-25	3	LAKEBED	172	0.455	7170.0	0.007	0.000	0.000
103	LRG-01	3	LAKEBED	116	0.139	1800.0	0.007	1.330	0.003
104	LRG-17	3	LAKEBED	91	0.968	3230.0	0.005	0.426	0.000
105	LRG-03	3	LAKEBED	118	0.262	2520.0	0.005	0.916	0.000
106	LRG-19	3	LAKEBED	93	1.790	8820.0	0.004	0.625	0.000
107	LRG-05	3	LAKEBED	120	0.234	2900.0	0.005	1.020	0.000
108	LRG-13	3	LAKEBED	128	6.570	35000.0	0.004	1.700	0.045
109	LRG-07	3	LAKEBED	122	0.622	6790.0	0.005	0.655	0.003
110	LRG-08	3	LAKEBED	123	0.284	3420.0	0.005	0.926	0.000
111	LRG-16	3	LAKEBED	131	1.200	4310.0	0.004	0.778	0.004
112	LRG-25	3	LAKEBED	99	0.959	3350.0	0.005	0.746	0.004
113	LRG-14	3	LAKEBED	129	2.530	10200.0	0.003	0.301	0.000
114	LRG-15	3	LAKEBED	130	1.560	4810.0	0.003	0.612	0.002
115	LRG-20	3	LAKEBED	94	2.220	13500.0	0.003	1.310	0.000
116	LRG-23	3	LAKEBED	97	4.680	27300.0	0.004	0.000	0.010

Data file 116PONDS
Title: CHEMICAL ANALYSES OF POND WATERS OF WESTERN SAN JOAQUIN VALLEY,CA

Function: PRLIST
Data case no. 1 to 30
Without selection

LIST OF VARIABLES

VAR	TYPE	NAME/DESCRIPTION
1	text 12	FIELD NUMBER
2	numeric	GEOLOGICAL ZONE
3	text 8	GEOLOGICAL ZONE
4	numeric	LAB. NUMBER
25	numeric	Se (ug L^{-1})/hydride
26	numeric	Si (mg L^{-1})/direct
27	numeric	Sr (mg L^{-1})/direct
28	numeric	U (mg L^{-1})/solvent ext.
29	numeric	V (mg L^{-1})/solvent ext.

CASE

NO.	1	2	3	4	25	26	27	28	29
1	ALT-01	1	ALLUVIAL	179	257.0	11.400	8.000	0.350	0.007
2	ALT-02	1	ALLUVIAL	180	265.0	4.980	8.300	0.454	0.010
3	ALT-03	1	ALLUVIAL	181	315.0	0.265	10.700	0.585	0.037
4	ALT-04	1	ALLUVIAL	182	1190.0	0.358	26.700	2.160	0.068
5	ALT-05	1	ALLUVIAL	183	339.0	0.708	10.300	0.681	0.020
6	ALT-06	1	ALLUVIAL	184	480.0	1.310	14.500	0.795	0.030
7	ALT-07	1	ALLUVIAL	185	306.0	4.370	9.360	0.561	0.016
8	ALT-17	1	ALLKUVIA	84	144.0	0.409	20.700	0.320	0.044
9	ALT-18	1	ALLUVIAL	85	3.0	0.450	20.900	0.404	0.053
10	ALT-19	1	ALLUVIAL	86	520.0	0.543	27.200	0.520	0.071
11	ALT-20	1	ALLUVIAL	87	553.0	0.735	32.800	0.522	0.071
12	HME-18	1	ALLUVIAL	165	112.0	0.724	20.800	0.152	0.040
13	ALT-22	1	ALLUVIAL	89	120.0	5.360	16.500	0.349	0.032
14	ALT-23	1	ALLUVIAL	90	119.0	3.240	15.500	0.307	0.040
15	BJG-04	1	ALLUVIAL	140	2060.0	0.528	17.400	0.706	0.023
16	BJG-05	1	ALLUVIAL	141	1260.0	3.170	11.000	0.465	0.019
17	BJG-06	1	ALLUVIAL	142	734.0	26.700	4.500	0.075	0.006
18	BJG-07	1	ALLUVIAL	143	762.0	14.700	5.550	0.136	0.010
19	BJG-08	1	ALLUVIAL	144	771.0	3.690	7.310	0.142	0.007
20	BJG-09	1	ALLUVIAL	145	683.0	0.966	8.250	0.243	0.007
21	BJG-10	1	ALLUVIAL	146	72.3	5.690	6.070	0.100	0.004
22	BJG-11	1	ALLUVIAL	147	74.6	5.010	5.490	0.090	0.003
23	HME-14	1	ALLUVIAL	81	183.0	6.840	14.900	0.222	0.036
24	HME-15	1	ALLUVIAL	82	151.0	19.600	7.560	0.139	0.023
25	HME-16	1	ALLUVIAL	83	157.0	5.940	14.200	0.211	0.037
26	HME-17	1	ALLUVIAL	164	82.9	4.530	15.900	0.246	0.030
27	EWJ-06	2	BASINRIM	105	1.0	5.380	5.250	0.054	0.007
28	BJG-01	2	BASINRIM	137	2.0	3.460	21.500	0.499	0.024
29	BJG-02	2	BASINRIM	138	12.4	7.390	8.460	0.149	0.013
30	EWJ-08	2	BASINRIM	107	4.1	18.000	5.800	0.097	0.035

Data file 116PONDS
Title: CHEMICAL ANALYSES OF POND WATERS OF WESTERN SAN JOAQUIN VALLEY,CA

Function: PRLIST
Data case no. 31 to 60
Without selection

LIST OF VARIABLES

VAR   TYPE   NAME/DESCRIPTION
  1   text 12   FIELD NUMBER
  2   numeric   GEOLOGICAL ZONE
  3   text 8   GEOLOGICAL ZONE
  4   numeric   LAB. NUMBER
 25   numeric   Se (ug L^-1)/hydride
 26   numeric   Si (mg L^-1)/direct
 27   numeric   Sr (mg L^-1)/direct
 28   numeric   U (mg L^-1)/solvent ext.
 29   numeric   V (mg L^-1)/solvent ext.

CASE

NO.		1	2	3	4	25	26	27	28	29
31	BY-01		2	BASINRIM	148	2.4	23.500	4.500	0.131	0.050
32	BY-02		2	BASINRIM	149	1.0	3.810	6.530	0.469	0.052
33	BY-03		2	BASINRIM	150	1.1	5.930	9.420	0.468	0.042
34	BY-04		2	BASINRIM	151	0.9	21.600	4.980	0.139	0.042
35	BY-05		2	BASINRIM	152	1.2	16.100	4.360	0.213	0.037
36	BY-06		2	BASINRIM	153	1.2	15.400	4.230	0.270	0.043
37	BY-07		2	BASINRIM	154	0.9	15.500	4.340	0.274	0.042
38	EWJ-01		2	BASINRIM	100	3.7	13.700	10.900	0.141	0.014
39	EWJ-02		2	BASINRIM	101	3.4	13.500	11.000	0.134	0.018
40	EWJ-03		2	BASINRIM	102	1.0	3.390	4.360	0.025	0.007
41	EWJ-04		2	BASINRIM	103	1.2	17.700	5.650	0.056	0.010
42	EWJ-05		2	BASINRIM	104	1.7	16.900	3.760	0.011	0.013
43	EWJ-21		2	BASINRIM	136	0.1	1.530	1.540	0.030	0.004
44	EWJ-07		2	BASINRIM	106	1.0	5.650	16.100	0.202	0.038
45	EWJ-15		2	BASINRIM	114	1.0	15.200	2.200	0.171	0.045
46	EWJ-09		2	BASINRIM	108	1.0	5.100	18.100	0.210	0.043
47	EWJ-10		2	BASINRIM	109	4.0	18.200	6.420	0.106	0.032
48	EWJ-11		2	BASINRIM	110	0.2	2.460	1.930	0.252	0.020
49	EWJ-19		2	BASINRIM	134	0.1	3.150	1.340	0.071	0.005
50	EWJ-13		2	BASINRIM	112	1.0	0.374	2.310	0.335	0.012
51	EWJ-14		2	BASINRIM	113	1.1	19.000	1.650	0.185	0.096
52	EWJ-18		2	BASAINRI	133	0.1	11.800	1.420	0.062	0.008
53	EWJ-16		2	BASINRIM	115	1.0	23.500	3.910	0.299	0.070
54	EWJ-17		2	BASINRIM	132	1.0	15.400	2.130	0.083	0.019
55	HME-11		3	LAKEBED	78	61.0	21.400	6.060	1.075	0.100
56	LRG-10		3	LAKEBED	125	1.4	15.100	0.535	0.040	0.194
57	LRG-18		3	LAKEBED	92	17.2	4.300	0.472	0.569	0.066
58	BY-15		3	LAKEBED	162	7.2	4.960	1.080	0.546	0.012
59	ALT-08		3	LAKEBED	186	2.5	14.700	3.460	0.956	0.108
60	ALT-09		3	LAKEBED	187	2.6	7.360	4.080	1.260	0.033

Data file **116PONDS**
Title: CHEMICAL ANALYSES OF POND WATERS OF WESTERN SAN JOAQUIN VALLEY,CA

Function: PRLIST
Data case no. 61 to 90
Without selection

LIST OF VARIABLES

VAR	TYPE	NAME/DESCRIPTION
1	text 12	FIELD NUMBER
2	numeric	GEOLOGICAL ZONE
3	text 8	GEOLOGICAL ZONE
4	numeric	LAB. NUMBER
25	numeric	Se (ug L^-1)/hydride
26	numeric	Si (mg L^-1)/direct
27	numeric	Sr (mg L^-1)/direct
28	numeric	U (mg L^-1)/solvent ext.
29	numeric	V (mg L^-1)/solvent ext.

CASE NO.	1	2	3	4	25	26	27	28	29
61	HME-10	3	LAKEBED	77	20.1	1.680	8.590	1.115	0.045
62	ALT-11	3	LAKEBED	189	0.0	10.000	13.800	9.900	0.206
63	ALT-12	3	LAKEBED	190	1.1	6.630	6.370	1.200	0.257
64	ALT-13	3	LAKEBED	191	0.0	11.100	6.930	2.140	0.544
65	ALT-14	3	LAKEBED	192	1.9	29.600	4.240	0.228	0.234
66	ALT-15	3	LAKEBED	193	2.1	30.000	4.500	0.238	0.220
67	ALT-16	3	LAKEBED	194	2.9	22.300	5.350	0.460	0.252
68	By-08	3	LAKEBED	155	3.6	5.520	1.530	1.380	0.017
69	BY-09	3	LAKEBED	156	6.1	4.070	1.160	1.025	0.020
70	BY-10	3	LAKEBED	157	4.8	4.580	0.845	1.145	0.014
71	BY-11	3	LAKEBED	158	1.5	3.260	0.961	1.343	0.017
72	BY-12	3	LAKEBED	159	7.7	2.660	0.927	1.145	0.014
73	LRG-02	3	LAKEBED	117	0.8	8.970	0.063	0.090	0.032
74	BY-14	3	LAKEBED	161	8.7	5.500	1.020	0.751	0.015
75	LRG-04	3	LAKEBED	119	1.2	14.100	0.480	0.062	0.135
76	BY-16	3	LAKEBED	163	8.9	7.280	1.020	0.474	0.018
77	BY-17	3	LAKEBED	173	8.7	6.650	0.719	0.730	0.030
78	BY-18	3	LAKEBED	174	11.8	12.100	1.280	0.496	0.051
79	BY-19	3	LAKEBED	175	10.7	12.100	0.920	0.382	0.033
80	BY-20	3	LAKEBED	176	1.3	8.250	1.770	2.590	0.025
81	HME-19	3	LAKEBED	166	1.4	3.860	13.300	0.269	0.014
82	BY-22	3	LAKEBED	178	1.3	9.910	6.620	0.392	0.040
83	HME-01	3	LAKEBED	68	5.6	8.210	4.630	1.030	0.084
84	HME-02	3	LAKEBED	69	7.7	9.550	3.280	0.643	0.140
85	HME-03	3	LAKEBED	70	8.6	25.400	7.330	0.515	0.185
86	HME-04	3	LAKEBED	71	7.2	9.410	3.230	0.674	0.139
87	HME-05	3	LAKEBED	72	11.5	21.000	15.200	0.332	0.140
88	HME-06	3	LAKEBED	73	8.9	2.820	15.700	0.461	0.020
89	HME-07	3	LAKEBED	74	23.5	0.075	20.100	0.241	0.030
90	HME-08	3	LAKEBED	75	17.1	0.665	11.800	0.525	0.022

Data file **116PONDS**
Title: CHEMICAL ANALYSES OF POND WATERS OF WESTERN SAN JOAQUIN VALLEY,CA

Function: PRLIST
Data case no. 91 to 116
Without selection

LIST OF VARIABLES

VAR	TYPE	NAME/DESCRIPTION
1	text 12	FIELD NUMBER
2	numeric	GEOLOGICAL ZONE
3	text 8	GEOLOGICAL ZONE
4	numeric	LAB. NUMBER
25	numeric	Se (ug L^{-1})/hydride
26	numeric	Si (mg L^{-1})/direct
27	numeric	Sr (mg L^{-1})/direct
28	numeric	U (mg L^{-1})/solvent ext.
29	numeric	V (mg L^{-1})/solvent ext.

CASE NO.	1	2	3	4	25	26	27	28	29
91	HME-09	3	LAKEBED	76	47.8	22.200	5.640	1.175	0.182
92	LRG-21	3	LAKEBED	95	6.0	3.990	0.618	1.690	0.023
93	LRG-06	3	LAKEBED	121	1.1	6.490	0.150	0.191	0.008
94	HME-12	3	LAKEBED	79	21.6	6.780	0.180	2.580	0.456
95	LRG-24	3	LAKEBED	98	0.4	0.278	1.480	1.950	0.051
96	LRG-09	3	LAKEBED	124	1.8	12.700	0.433	0.061	0.170
97	HME-20	3	LAKEBED	167	2.2	1.340	11.900	0.133	0.006
98	HME-21	3	LAKEBED	168	2.7	0.000	6.830	0.162	0.004
99	LRG-12	3	LAKEBED	127	1.7	17.900	0.632	0.049	0.220
100	HME-23	3	LAKEBED	170	4.4	7.050	6.190	0.170	0.010
101	HME-24	3	LAKEBED	171	6.1	4.850	7.000	0.156	0.012
102	HME-25	3	LAKEBED	172	12.2	4.900	6.030	0.138	0.010
103	LRG-01	3	LAKEBED	116	2.5	17.800	0.830	0.108	0.165
104	LRG-17	3	LAKEBED	91	22.2	10.800	0.778	0.396	0.071
105	LRG-03	3	LAKEBED	118	0.8	10.400	0.502	0.133	0.050
106	LRG-19	3	LAKEBED	93	9.0	9.710	0.460	0.879	0.034
107	LRG-05	3	LAKEBED	120	1.7	8.190	0.360	0.145	0.021
108	LRG-13	3	LAKEBED	128	1.5	23.400	1.720	2.660	0.027
109	LRG-07	3	LAKEBED	122	1.0	8.280	0.127	0.228	0.007
110	LRG-08	3	LAKEBED	123	1.5	12.100	0.187	0.117	0.032
111	LRG-16	3	LAKEBED	131	16.1	7.050	0.406	0.530	0.042
112	LRG-25	3	LAKEBED	99	27.7	13.900	2.190	0.493	0.078
113	LRG-14	3	LAKEBED	129	7.9	6.190	0.969	1.023	0.018
114	LRG-15	3	LAKEBED	130	9.2	5.530	0.424	0.326	0.018
115	LRG-20	3	LAKEBED	94	1.9	9.070	0.524	1.220	0.022
116	LRG-23	3	LAKEBED	97	22.1	0.220	2.110	2.420	0.053

Data file 116PONDS
Title: CHEMICAL ANALYSES OF POND WATERS OF WESTERN SAN JOAQUIN VALLEY,CA

Function: PRLIST
Data case no. 1 to 30
Without selection

LIST OF VARIABLES

VAR	TYPE	NAME/DESCRIPTION
1	text 12	FIELD NUMBER
2	numeric	GEOLOGICAL ZONE
3	text 8	GEOLOGICAL ZONE
4	numeric	LAB. NUMBER
30	numeric	Zn (mg L^-1)/solvent ext.
31	numeric	SO4 (meq L^-1)
32	numeric	Cl (meq L^-1)
33	numeric	Alkalinity (meq L^-1)

CASE NO.	1	2	3	4	30	31	32	33
1	ALT-01	1	ALLUVIAL	179	0.002	306.3	62.8	9.7
2	ALT-02	1	ALLUVIAL	180	0.001	330.8	62.8	8.6
3	ALT-03	1	ALLUVIAL	181	0.005	476.1	96.5	11.0
4	ALT-04	1	ALLUVIAL	182	0.000	1899.4	505.6	32.4
5	ALT-05	1	ALLUVIAL	183	0.006	505.3	104.8	10.9
6	ALT-06	1	ALLUVIAL	184	0.002	799.3	182.9	18.1
7	ALT-07	1	ALLUVIAL	185	0.003	371.2	75.3	9.2
8	ALT-17	1	ALLKUVIA	84	0.004	506.2	913.7	13.3
9	ALT-18	1	ALLUVIAL	85	0.003	468.8	860.4	12.9
10	ALT-19	1	ALLUVIAL	86	0.000	618.0	1415.0	15.5
11	ALT-20	1	ALLUVIAL	87	0.000	657.3	1767.6	15.6
12	HME-18	1	ALLUVIAL	165	0.004	444.7	928.9	11.2
13	ALT-22	1	ALLUVIAL	89	0.003	593.9	777.9	10.2
14	ALT-23	1	ALLUVIAL	90	0.008	333.0	548.9	8.6
15	BJG-04	1	ALLUVIAL	140	0.024	589.3	181.1	13.3
16	BJG-05	1	ALLUVIAL	141	0.005	436.9	119.8	14.0
17	BJG-06	1	ALLUVIAL	142	0.007	97.3	24.9	13.2
18	BJG-07	1	ALLUVIAL	143	0.004	145.4	39.5	12.6
19	BJG-08	1	ALLUVIAL	144	0.032	205.2	62.7	30.4
20	BJG-09	1	ALLUVIAL	145	0.005	270.6	68.5	22.2
21	BJG-10	1	ALLUVIAL	146	0.036	268.4	31.0	23.2
22	BJG-11	1	ALLUVIAL	147	0.006	280.3	33.3	18.7
23	HME-14	1	ALLUVIAL	81	0.004	248.6	327.7	9.3
24	HME-15	1	ALLUVIAL	82	0.004	123.5	150.2	6.5
25	HME-16	1	ALLUVIAL	83	0.000	249.4	350.6	8.2
26	HME-17	1	ALLUVIAL	164	0.008	225.2	471.6	6.9
27	EWJ-06	2	BASINRIM	105	0.017	331.0	45.1	8.7
28	BJG-01	2	BASINRIM	137	0.016	1950.1	970.6	0.4
29	BJG-02	2	BASINRIM	138	0.006	587.3	121.0	0.2
30	EWJ-08	2	BASINRIM	107	0.010	276.6	23.1	9.5

Data file 116PONDS
Title: CHEMICAL ANALYSES OF POND WATERS OF WESTERN SAN JOAQUIN VALLEY,CA

Function: PRLIST
Data case no. 31 to 60
Without selection

LIST OF VARIABLES

VAR   TYPE   NAME/DESCRIPTION
  1   text 12   FIELD NUMBER
  2   numeric   GEOLOGICAL ZONE
  3   text 8   GEOLOGICAL ZONE
  4   numeric   LAB. NUMBER
 30   numeric   Zn (mg L^-1)/solvent ext.
 31   numeric   SO4 (meq L^-1)
 32   numeric   Cl (meq L^-1)
 33   numeric   Alkalinity (meq L^-1)

CASE
NO.   1   2   3   4   30   31   32   33
----
  31   BY-01   2 BASINRIM 148   0.002   313.1   55.1   40.2
  32   BY-02   2 BASINRIM 149   0.009 1271.6   237.0   39.5
  33   BY-03   2 BASINRIM 150   0.007 1571.7   296.5   39.6
  34   BY-04   2 BASINRIM 151   0.027   359.3   61.7   5.1
  35   BY-05   2 BASINRIM 152   0.005   579.2   104.9   5.1
  36   BY-06   2 BASINRIM 153   0.008   584.8   102.6   5.7
  37   BY-07   2 BASINRIM 154   0.011   588.9   115.4   7.0
  38   EWJ-01   2 BASINRIM 100   0.003 1147.5   241.4   9.7
  39   EWJ-02   2 BASINRIM 101   0.008   158.3   9.3
  40   EWJ-03   2 BASINRIM 102   0.005   362.2   53.0   5.7
  41   EWJ-04   2 BASINRIM 103   0.007   277.6   35.7   25.8
  42   EWJ-05   2 BASINRIM 104   0.002   109.3   15.0   24.7
  43   EWJ-21   2 BASINRIM 136   0.005   208.4   58.5   0.6
  44   EWJ-07   2 BASINRIM 106   0.003   552.1   28.7
  45   EWJ-15   2 BASINRIM 114   0.025   168.4   103.8   13.0
  46   EWJ-09   2 BASINRIM 108   0.003   572.1   10.1
  47   EWJ-10   2 BASINRIM 109   0.006   328.4   30.7   10.3
  48   EWJ-11   2 BASINRIM 110   0.008   266.1   138.1   11.6
  49   EWJ-19   2 BASINRIM 134   0.006   159.1   49.1   0.8
  50   EWJ-13   2 BASINRIM 112   0.007   343.0   169.9   12.7
  51   EWJ-14   2 BASINRIM 113   0.006   76.8   56.7   9.8
  52   EWJ-18   2 BASAINRI 133   0.006   136.1   44.7   0.3
  53   EWJ-16   2 BASINRIM 115   0.007   164.5   83.9   16.1
  54   EWJ-17   2 BASINRIM 132   0.005   75.4   23.7   1.0
  55   HME-11   3 LAKEBED   78   0.001   136.4   161.6   8.4
  56   LRG-10   3 LAKEBED   125   0.005   17.3   22.6   31.1
  57   LRG-18   3 LAKEBED   92   0.006   109.1   104.8   9.0
  58   BY-15   3 LAKEBED   162   0.012   187.0   215.2   5.0
  59   ALT-08   3 LAKEBED   186   0.004   119.7   163.0   10.8
  60   ALT-09   3 LAKEBED   187   0.000   168.5   243.0   10.7

Data file 116PONDS
Title: CHEMICAL ANALYSES OF POND WATERS OF WESTERN SAN JOAQUIN VALLEY,CA

Function: PRLIST
Data case no. 61 to 90
Without selection

LIST OF VARIABLES

VAR	TYPE	NAME/DESCRIPTION
1	text 12	FIELD NUMBER
2	numeric	GEOLOGICAL ZONE
3	text 8	GEOLOGICAL ZONE
4	numeric	LAB. NUMBER
30	numeric	Zn (mg L^-1)/solvent ext.
31	numeric	SO4 (meq L^-1)
32	numeric	Cl (meq L^-1)
33	numeric	Alkalinity (meq L^-1)

CASE NO.	1	2	3	4	30	31	32	33
61	HME-10	3	LAKEBED	77	0.000	311.8	315.3	9.2
62	ALT-11	3	LAKEBED	189	0.013	1191.4	2564.3	29.0
63	ALT-12	3	LAKEBED	190	0.000	394.3	540.8	19.4
64	ALT-13	3	LAKEBED	191	0.000	906.9	1357.0	44.2
65	ALT-14	3	LAKEBED	192	0.001	83.1	154.7	6.8
66	ALT-15	3	LAKEBED	193	0.002	97.9	156.6	19.8
67	ALT-16	3	LAKEBED	194	0.000	117.6	267.5	12.7
68	By-08	3	LAKEBED	155	0.006	558.3	467.9	8.1
69	BY-09	3	LAKEBED	156	0.006	366.2	297.6	8.1
70	BY-10	3	LAKEBED	157	0.011	397.1	358.6	10.0
71	BY-11	3	LAKEBED	158	0.010	608.9	579.9	20.1
72	BY-12	3	LAKEBED	159	0.000	467.3	395.2	19.8
73	LRG-02	3	LAKEBED	117	0.010	50.9	26.8	13.9
74	BY-14	3	LAKEBED	161	0.011	268.1	302.8	4.9
75	LRG-04	3	LAKEBED	119	0.010	36.4	21.6	21.3
76	BY-16	3	LAKEBED	163	0.009	143.8	151.4	6.5
77	BY-17	3	LAKEBED	173	0.007	237.8	272.5	13.7
78	BY-18	3	LAKEBED	174	0.007	113.4	132.5	9.2
79	BY-19	3	LAKEBED	175	0.007	118.8	131.0	7.8
80	BY-20	3	LAKEBED	176	0.000	1282.4	1268.4	29.8
81	HME-19	3	LAKEBED	166	0.008	855.9	848.1	17.5
82	BY-22	3	LAKEBED	178	0.005	226.0	262.8	11.9
83	HME-01	3	LAKEBED	68	0.004	589.7	893.2	15.0
84	HME-02	3	LAKEBED	69	0.004	359.9	560.2	13.4
85	HME-03	3	LAKEBED	70	0.002	168.8	293.0	11.4
86	HME-04	3	LAKEBED	71	0.005	305.5	559.4	13.6
87	HME-05	3	LAKEBED	72	0.000	282.0	614.0	11.3
88	HME-06	3	LAKEBED	73	0.000	302.9	634.7	7.2
89	HME-07	3	LAKEBED	74	0.000	500.4	983.7	8.0
90	HME-08	3	LAKEBED	75	0.000	288.9	523.4	6.9

Data file **116PONDS**
Title: CHEMICAL ANALYSES OF POND WATERS OF WESTERN SAN JOAQUIN VALLEY,CA

Function: PRLIST
Data case no. 91 to 116
Without selection

LIST OF VARIABLES

VAR	TYPE	NAME/DESCRIPTION
1	text 12	FIELD NUMBER
2	numeric	GEOLOGICAL ZONE
3	text 8	GEOLOGICAL ZONE
4	numeric	LAB. NUMBER
30	numeric	Zn (mg L^-1)/solvent ext.
31	numeric	SO4 (meq L^-1)
32	numeric	Cl (meq L^-1)
33	numeric	Alkalinity (meq L^-1)

CASE NO.	1	2	3	4	30	31	32	33
91	HME-09	3	LAKEBED	76	0.001	124.3	216.3	8.7
92	LRG-21	3	LAKEBED	95	0.004	785.6	585.2	28.5
93	LRG-06	3	LAKEBED	121	0.012	82.0	32.0	17.5
94	HME-12	3	LAKEBED	79	0.000	401.9	388.5	46.5
95	LRG-24	3	LAKEBED	98	0.004	539.2	590.5	14.4
96	LRG-09	3	LAKEBED	124	0.008	25.2	23.9	14.4
97	HME-20	3	LAKEBED	167	0.005	590.8	536.4	12.3
98	HME-21	3	LAKEBED	168	0.008	255.8	321.3	7.8
99	LRG-12	3	LAKEBED	127	0.005	16.4	22.8	15.4
100	HME-23	3	LAKEBED	170	0.005	165.4	145.6	5.2
101	HME-24	3	LAKEBED	171	0.004	214.8	211.5	6.8
102	HME-25	3	LAKEBED	172	0.005	200.3	222.7	6.4
103	LRG-01	3	LAKEBED	116	0.010	42.1	23.4	15.4
104	LRG-17	3	LAKEBED	91	0.008	83.8	81.5	7.8
105	LRG-03	3	LAKEBED	118	0.010	53.8	29.8	18.4
106	LRG-19	3	LAKEBED	93	0.003	205.6	212.6	13.3
107	LRG-05	3	LAKEBED	120	0.008	62.6	27.2	32.4
108	LRG-13	3	LAKEBED	128	0.080	505.6	1745.6	9.0
109	LRG-07	3	LAKEBED	122	0.004	158.9	115.0	14.8
110	LRG-08	3	LAKEBED	123	0.012	75.7	49.7	13.4
111	LRG-16	3	LAKEBED	131	0.006	117.3	83.5	0.8
112	LRG-25	3	LAKEBED	99	0.009	97.6	85.8	13.1
113	LRG-14	3	LAKEBED	129	0.004	260.6	458.2	38.9
114	LRG-15	3	LAKEBED	130	0.005	111.5	105.5	0.3
115	LRG-20	3	LAKEBED	94	0.003	359.6	349.2	17.9
116	LRG-23	3	LAKEBED	97	0.002	639.8	619.3	16.9

Data file   S P I K E S
Title: SPIKED DUPLICATES OF POND WATER SAMPLES, W. SAN JOAQUIN VALLEY CA

Function: PRLIST
Data case no. 1 to 25
Without selection

LIST OF VARIABLES

VAR   TYPE   NAME/DESCRIPTION
  1   text 12   FIELD No. AND STATISTICS
  4   numeric   LAB. NUMBER
  7   numeric   Al (mg L^-1)/direct
  8   numeric   As (ug L^-1)/hydride
  9   numeric   B (mg L^-1)/direct
 10   numeric   Ba (mg L^-1)/direct
 11   numeric   Ca (mg L^-1)/direct

CASE
NO.   1   4   7   8   9   10   11
----
   1   EWJ-11   110   0.000   25.0   15.00   0.000   153.00
   2   SPIKED   0.000   50.0   0.00   0.000   0.00
   3   EXPECTED   0.000   75.0   15.00   0.000   153.00
   4   EWJ-12   111   0.000   56.4   14.40   0.000   151.00
   5   ------------
   6   EWJ-19   134   0.523   7.0   6.34   0.000   144.00
   7   SPIKED   0.000   10.0   0.00   0.000   0.00
   8   EXPEXTED   0.523   17.0   6.34   0.000   144.00
   9   EWJ-20   135   0.531   14.1   6.50   0.000   152.00
  10   ------------
  11   LRG-10   125   0.000   128.0   3.46   0.000   42.40
  12   SPIKED   0.000   170.0   0.00   0.000   0.00
  13   EXPECTED   0.000   298.0   3.46   0.000   42.40
  14   LRG-11   126   0.000   253.0   3.20   0.000   42.40
  15   ------------
  16   LRG-21   95   0.000   354.0   49.60   0.000   80.20
  17   SPIKED   0.000   500.0   0.00   0.000   0.00
  18   EXPECTED   0.000   854.0   49.60   0.000   80.20
  19   LRG-22   96   0.000   764.0   54.00   0.000   68.20
  20   ------------
  21   BY-12   159   0.000   218.0   36.20   0.000   84.40
  22   SPIKED   0.000   300.0   0.00   0.000   0.00
  23   EXPECTED   0.000   518.0   36.20   0.000   84.40
  24   BY-13   160   0.000   386.0   35.30   0.000   82.20
  25   ------------

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Data file    SPIKES
Title: SPIKED DUPLICATES OF POND WATER SAMPLES, W. SAN JOAQUIN VALLEY CA

Function: PRLIST
Data case no.  1  to  25
Without selection


LIST OF VARIABLES
------------------


VAR   TYPE       NAME/DESCRIPTION
  1   text 12    FIELD No. AND STATISTICS
  4   numeric    LAB. NUMBER
 12   numeric    Cd (mg L^-1)/solvent ext.
 13   numeric    Cr (mg L^-1)/solvent ext.
 14   numeric    Cu (mg L^-1)/solvent ext.
 15   numeric    Fe (mg L^-1)/solvent ext.
 16   numeric    K  (mg L^-1)/direct

CASE
NO.              1     4      12      13      14      15      16
------------------------------------------------------------------
    1   EWJ-11        110   0.000   0.000   0.004   0.012   17.80
    2   SPIKED              0.010   0.010   0.010   0.000    0.00
    3   EXPECTED            0.010   0.010   0.014   0.012   17.80
    4   EWJ-12        111   0.011   0.000   0.011   0.013   16.80
    5   -----------
    6   EWJ-19        134   0.000   0.000   0.008   0.015   12.50
    7   SPIKED              0.010   0.010   0.010   0.000    0.00
    8   EXPEXTED            0.010   0.010   0.018   0.015   12.50
    9   EWJ-20        135   0.016   0.000   0.019   0.014   13.40
   10   -----------
   11   LRG-10        125   0.000   0.000   0.012   0.020    3.14
   12   SPIKED              0.010   0.010   0.010   0.000    0.00
   13   EXPECTED            0.010   0.010   0.022   0.020    3.14
   14   LRG-11        126   0.012   0.000   0.022   0.014    3.06
   15   -----------
   16   LRG-21         95   0.000   0.000   0.001   0.024  101.00
   17   SPIKED              0.010   0.010   0.010   0.000    0.00
   18   EXPECTED            0.010   0.010   0.011   0.024  101.00
   19   LRG-22         96   0.015   0.000   0.012   0.021   92.50
   20   -----------
   21   BY-12         159   0.000   0.000   0.004   0.051   52.30
   22   SPIKED              0.010   0.010   0.010   0.000    0.00
   23   EXPECTED            0.010   0.010   0.014   0.051   52.30
   24   BY-13         160   0.013   0.000   0.010   0.032   46.00
   25   -----------
------------------------------------------------------------------
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Data file   S P I K E S
Title: SPIKED DUPLICATES OF POND WATER SAMPLES, W. SAN JOAQUIN VALLEY CA

Function: PRLIST
Data case no. 1 to 25
Without selection

LIST OF VARIABLES

VAR	TYPE	NAME/DESCRIPTION
1	text 12	FIELD No. AND STATISTICS
4	numeric	LAB. NUMBER
17	numeric	Li (mg L^-1)/direct
18	numeric	Mg (mg L^-1)/direct
19	numeric	Mn (mg L^-1)/solvent ext.
20	numeric	Mo (mg L^-1)/direct
21	numeric	Na (mg L^-1)/direct

CASE NO.		1	4	17	18	19	20	21
1	EWJ-11		110	0.000	604.0	0.001	0.768	8950.0
2	SPIKED			0.000	0.0	0.000	0.000	0.0
3	EXPECTED			0.000	604.0	0.001	0.768	8950.0
4	EWJ-12		111	0.000	615.0	0.000	0.842	9040.0
5	-----------							
6	EWJ-19		134	0.000	455.0	0.012	0.281	4420.0
7	SPIKED			0.000	0.0	0.000	0.000	0.0
8	EXPEXTED			0.000	455.0	0.012	0.281	4420.0
9	EWJ-20		135	0.000	464.0	0.008	0.289	4510.0
10	-----------							
11	LRG-10		125	0.000	51.6	0.008	0.138	1590.0
12	SPIKED			0.000	0.0	0.000	0.000	0.0
13	EXPECTED			0.000	51.6	0.008	0.138	1590.0
14	LRG-11		126	0.000	55.5	0.008	0.153	1570.0
15	-----------							
16	LRG-21		95	0.707	1830.0	0.001	3.520	28400.0
17	SPIKED			0.000	0.0	0.000	0.000	0.0
18	EXPECTED			0.707	1830.0	0.001	3.520	28400.0
19	LRG-22		96	0.535	1990.0	0.000	3.230	31200.0
20	-----------							
21	BY-12		159	0.172	1030.0	0.014	2.820	17500.0
22	SPIKED			0.000	0.0	0.000	0.000	0.0
23	EXPECTED			0.172	1030.0	0.014	2.820	17500.0
24	BY-13		160	0.282	1000.0	0.006	2.940	17000.0
25	-----------							

Data file   SPIKES
Title: SPIKED DUPLICATES OF POND WATER SAMPLES, W. SAN JOAQUIN VALLEY CA

Function: PRLIST
Data case no. 1 to 25
Without selection

LIST OF VARIABLES

VAR	TYPE	NAME/DESCRIPTION
1	text 12	FIELD No. AND STATISTICS
4	numeric	LAB. NUMBER
22	numeric	Ni (mg L^-1)/solvent ext.
23	numeric	P (mg L^-1)/direct
24	numeric	Pb (mg L^-1)/solvent ext.
25	numeric	Se (ug L^-1)/hydride
26	numeric	Si (mg L^-1)/direct

CASE

NO.	1	4	22	23	24	25	26
1	EWJ-11	110	0.003	0.000	0.000	0.0	2.460
2	SPIKED		0.020	0.000	0.020	0.0	0.000
3	EXPECTED		0.023	0.000	0.020	0.0	2.460
4	EWJ-12	111	0.017	0.000	0.000	0.0	2.630
5	------------						
6	EWJ-19	134	0.005	0.000	0.005	0.0	3.150
7	SPIKED		0.020	0.000	0.010	0.0	0.000
8	EXPEXTED		0.025	0.000	0.015	0.0	3.150
9	EWJ-20	135	0.027	0.000	0.009	0.0	3.190
10	------------						
11	LRG-10	125	0.004	1.110	0.001	1.4	15.100
12	SPIKED		0.010	0.000	0.010	0.0	0.000
13	EXPECTED		0.014	1.110	0.011	1.4	15.100
14	LRG-11	126	0.016	1.300	0.006	1.8	15.100
15	------------						
16	LRG-21	95	0.002	0.000	0.000	6.0	3.990
17	SPIKED		0.010	0.000	0.010	0.0	3.640
18	EXPECTED		0.012	0.000	0.010	6.0	0.000
19	LRG-22	96	0.012	0.000	0.000	8.1	3.990
20	------------						
21	BY-12	159	0.007	0.000	0.000	7.7	2.660
22	SPIKED		0.010	0.000	0.010	0.0	0.000
23	EXPECTED		0.017	0.000	0.010	7.7	2.660
24	BY-13	160	0.012	0.000	0.000	12.4	2.670
25	------------						

Data file   SPIKES
Title: SPIKED DUPLICATES OF POND WATER SAMPLES, W. SAN JOAQUIN VALLEY CA

Function: PRLIST
Data case no. 1 to 25
Without selection

LIST OF VARIABLES

VAR	TYPE	NAME/DESCRIPTION
1	text 12	FIELD No. AND STATISTICS
4	numeric	LAB. NUMBER
27	numeric	Sr (mg L^-1)/direct
28	numeric	U (mg L^-1)/solvent ext.
29	numeric	V (mg L^-1)/solvent ext.
30	numeric	Zn (mg L^-1)/solvent ext.

CASE

NO.		1	4	27	28	29	30
1	EWJ-11		110	1.930	0.252	0.020	0.008
2	SPIKED			0.000	0.000	0.100	0.030
3	EXPECTED			1.930	0.252	0.120	0.038
4	EWJ-12		111	1.830	0.200	0.116	0.025
5	------------						
6	EWJ-19		134	1.330	0.071	0.005	0.006
7	SPIKED			0.000	0.050	0.100	0.010
8	EXPEXTED			1.330	0.121	0.105	0.016
9	EWJ-20		135	1.330	0.060	0.110	0.016
10	------------						
11	LRG-10		125	0.535	0.040	0.194	0.005
12	SPIKED			0.000	0.050	0.100	0.010
13	EXPECTED			0.535	0.090	0.294	0.015
14	LRG-11		126	0.545	0.145	0.307	0.011
15	------------						
16	LRG-21		95	0.618	1.690	0.023	0.004
17	SPIKED			0.000	0.000	0.100	0.010
18	EXPECTED			0.527	1.690	0.123	0.014
19	LRG-22		96	0.618	1.700	0.100	0.020
20	------------						
21	BY-12		159	0.927	1.145	0.014	0.000
22	SPIKED			0.000	0.000	0.100	0.010
23	EXPECTED			0.927	1.145	0.114	0.010
24	BY-13		160	0.937	0.950	0.083	0.018
25	------------						

Data file   DUPLICS
Title: BLIND DUPLICATES OF POND WATER SAMPLES, W. SAN JOAQUIN VALLEY CA.

Function: PRLIST
Data case no. 1 to 30
Without selection

LIST OF VARIABLES

VAR   TYPE   NAME/DESCRIPTION
  1   text 12   FIELD No. AND STATISTICS
  4   numeric   LAB. NUMBER
  7   numeric   Al (mg L^-1)/direct
  8   numeric   As (ug L^-1)/hydride
  9   numeric   B (mg L^-1)/direct
 10   numeric   Ba (mg L^-1)/direct
 11   numeric   Ca (mg L^-1)/direct

CASE
NO.   1   4   7   8   9   10   11
----
   1   ALT-20   87 1120.00   19.9   171.00   0.102   545.00
   2   ALT-21   88 2810.00   18.7   233.00   0.110   744.00
   3   MEAN   19.3   202.00   0.106   644.50
   4   %DEV/MEAN   3.1   15.30   3.780   15.40
   5   -----------
   6   BJG-02   138   0.00   3.3   38.10   0.000   531.00
   7   BJG-3   139   327.00   2.8   42.00   0.000   578.00
   8   MEAN   3.1   40.05   554.50
   9   %DEV/MEAN   8.2   4.87   4.20
  10   -----------
  11   ALT-10   188   1.20 4260.0   387.00   0.024   230.00
  12   ALT-11   189   1.07 4490.0   392.00   0.012   279.00
  13   MEAN   1.13 4375.0   389.50   0.018   254.50
  14   %DEV/MEAN   5.72   2.6   0.64   33.333   9.62
  15   -----------
  16   BY-20   176   776.00   497.0   125.00   0.023   178.00
  17   BY-21   177   370.00   505.0   107.00   0.033   160.00
  18   MEAN   573.00   501.0   116.00   0.028   169.00
  19   %DEV/MEAN   35.43   0.8   7.76   17.900   5.32
  20   -----------
  21   HME-12   79   0.00 2600.0   57.60   0.000   8.90
  22   HME-13   80   416.00 2250.0   62.60   0.017   6.80
  23   MEAN   2425.0   60.10   7.85
  24   %DEV/MEAN   7.2   4.15   13.37
  25   -----------
  26   HME-21   168   0.00   14.0   20.40   0.000   626.00
  27   HME-22   169   807.00   14.3   20.20   0.008   615.00
  28   MEAN   14.1   20.30   620.50
  29   %DEV/MEAN   1.1   0.49   0.89
  30   -----------

Data file DUPLICS
Title: BLIND DUPLICATES OF POND WATER SAMPLES, W. SAN JOAQUIN VALLEY CA.

Function: PRLIST
Data case no. 1 to 30
Without selection

LIST OF VARIABLES

VAR   TYPE   NAME/DESCRIPTION
  1   text 12   FIELD No. AND STATISTICS
  4   numeric   LAB. NUMBER
 12   numeric   Cd (mg L^-1)/solvent ext.
 13   numeric   Cr (mg L^-1)/solvent ext.
 14   numeric   Cu (mg L^-1)/solvent ext.
 15   numeric   Fe (mg L^-1)/solvent ext.
 16   numeric   K (mg L^-1)/direct

CASE
NO.   1   4   12   13   14   15   16
----

  1   ALT-20   87   0.000   0.000   0.007   0.006   43.10
  2   ALT-21   88   0.000   0.000   0.007   0.006   41.80
  3   MEAN   0.007   0.006   42.45
  4   %DEV/MEAN   0.000   0.000   1.53
  5   --------------
  6   BJG-02   138   0.000   0.005   0.010   0.007   10.40
  7   BJG-3   139   0.000   0.007   0.008   0.008   11.50
  8   MEAN   0.006   0.009   0.007   10.95
  9   %DEV/MEAN   16.670   11.100   6.670   5.02
 10   --------------
 11   ALT-10   188   0.000   0.000   0.000   0.035   149.00
 12   ALT-11   189   0.000   0.000   0.005   0.038   151.00
 13   MEAN   0.003   0.037   150.00
 14   %DEV/MEAN   67.000   4.109   0.67
 15   --------------
 16   BY-20   176   0.000   0.001   0.002   0.032   197.00
 17   BY-21   177   0.000   0.001   0.002   0.027   219.00
 18   MEAN   0.002   0.030   208.00
 19   %DEV/MEAN   0.000   8.470   5.29
 20   --------------
 21   HME-12   79   0.000   0.000   0.009   0.027   109.00
 22   HME-13   80   0.000   0.000   0.009   0.021   108.00
 23   MEAN   0.009   0.024   108.50
 24   %DEV/MEAN   0.000   12.500   0.46
 25   --------------
 26   HME-21   168   0.000   0.000   0.007   0.010   69.60
 27   HME-22   169   0.000   0.000   0.003   0.050   68.10
 28   MEAN   0.005   0.030   68.85
 29   %DEV/MEAN   40.000   66.667   1.09
 30   --------------

Data file DUPLICS
Title: BLIND DUPLICATES OF POND WATER SAMPLES, W. SAN JOAQUIN VALLEY CA.

Function: PRLIST
Data case no. 1 to 30
Without selection

LIST OF VARIABLES

VAR TYPE   NAME/DESCRIPTION
  1 text 12   FIELD No. AND STATISTICS
  4 numeric   LAB. NUMBER
 17 numeric   Li (mg L^-1)/direct
 18 numeric   Mg (mg L^-1)/direct
 19 numeric   Mn (mg L^-1)/solvent ext.
 20 numeric   Mo (mg L^-1)/direct
 21 numeric   Na (mg L^-1)/direct

CASE

NO.		1	4	17	18	19	20	21
1	ALT-20		87	1.420	1280.0	0.000	4.230	34400.0
2	ALT-21		88	1.260	1270.0	0.000	3.550	46000.0
3	MEAN			1.340	1275.0		3.890	40200.0
4	%DEV/MEAN			5.970	0.4		8.740	14.4
5	-----------							
6	BJG-02		138	0.240	2310.0	0.000	0.455	15400.0
7	BJG-3		139	0.230	2510.0	0.000	0.538	17100.0
8	MEAN			0.235	2410.0		0.497	16250.0
9	%DEV/MEAN			2.130	4.0		8.350	5.2
10	-----------							
11	ALT-10		188	4.300	1290.0	0.000	25.600	77600.0
12	ALT-11		189	4.100	1370.0	0.000	23.700	76100.0
13	MEAN			4.200	1330.0		24.650	76850.0
14	%DEV/MEAN			2.380	2.9		3.850	1.0
15	-----------							
16	BY-20		176	1.640	3420.0	0.000	8.050	54400.0
17	BY-21		177	1.610	2990.0	0.000	8.070	47000.0
18	MEAN			1.630	3205.0	0.000	8.060	50700.0
19	%DEV/MEAN			0.920	6.7	0.000	0.110	7.3
20	-----------							
21	HME-12		79	0.321	335.0	0.000	4.650	21900.0
22	HME-13		80	0.361	381.0	0.000	4.690	23600.0
23	MEAN			0.341	358.0		4.670	22750.0
24	%DEV/MEAN			5.870	6.4		0.430	3.7
25	-----------							
26	HME-21		168	0.276	1340.0	0.011	0.508	10200.0
27	HME-22		169	0.349	1310.0	0.020	0.537	10000.0
28	MEAN			0.313	1325.0	0.016	0.523	10100.0
29	%DEV/MEAN			11.670	1.1	29.030	2.770	1.0
30	-----------							

Data file DUPLICS
Title: BLIND DUPLICATES OF POND WATER SAMPLES, W. SAN JOAQUIN VALLEY CA.

Function: PRLIST
Data case no. 1 to 30
Without selection

LIST OF VARIABLES

```
VAR   TYPE        NAME/DESCRIPTION
  1   text 12     FIELD No. AND STATISTICS
  4   numeric     LAB. NUMBER
 22   numeric     Ni (mg L^-1)/solvent ext.
 23   numeric     P (mg L^-1)/direct
 24   numeric     Pb (mg L^-1)/solvent ext.
 25   numeric     Se (ug L^-1)/hydride
 26   numeric     Si (mg L^-1)/direct
```

CASE

NO.		1	4	22	23	24	25	26
1	ALT-20		87	0.006	0.000	0.032	553.0	0.735
2	ALT-21		88	0.006	0.000	0.000	540.0	0.873
3	MEAN			0.006			546.5	0.804
4	%DEV/MEAN			0.000			1.2	8.580
5	----------							
6	BJG-02		138	0.008	0.000	0.004	12.4	7.390
7	BJG-3		139	0.010	0.000	0.000	11.8	7.480
8	MEAN			0.009			12.1	7.435
9	%DEV/MEAN			11.100			2.5	0.605
10	----------							
11	ALT-10		188	0.002	0.000	0.070	1.1	10.500
12	ALT-11		189	0.009	0.000	0.100	0.0	10.000
13	MEAN			0.006		0.089	0.6	10.250
14	%DEV/MEAN			63.636		17.650	100.0	2.490
15	----------							
16	BY-20		176	0.002	0.000	0.061	1.3	8.250
17	BY-21		177	0.001	0.000	0.000	1.0	8.300
18	MEAN			0.002			1.1	8.275
19	%DEV/MEAN			33.000			13.0	0.302
20	----------							
21	HME-12		79	0.009	0.564	0.010	21.6	6.780
22	HME-13		80	0.008	0.903	0.000	39.8	6.920
23	MEAN			0.009	0.733		30.7	6.850
24	%DEV/MEAN			5.880	23.000		29.6	1.021
25	----------							
26	HME-21		168	0.011	0.000	0.000	2.7	0.000
27	HME-22		169	0.009	0.000	0.000	2.5	0.000
28	MEAN			0.010			2.6	0.000
29	%DEV/MEAN			10.000			3.8	0.000
30	----------							

```
Data file   DUPLICS
Title: BLIND DUPLICATES OF POND WATER SAMPLES, W. SAN JOAQUIN VALLEY CA.

Function: PRLIST
Data case no.  1  to  30
Without selection


LIST OF VARIABLES
----------------

VAR   TYPE       NAME/DESCRIPTION
  1   text 12    FIELD No. AND STATISTICS
  4   numeric    LAB. NUMBER
 27   numeric    Sr (mg L^-1)/direct
 28   numeric    U (mg L^-1)/solvent ext.
 29   numeric    V (mg L^-1)/solvent ext.
 30   numeric    Zn (mg L^-1)/solvent ext.

CASE
NO.             1     4      27       28       29       30
------------------------------------------------------------------
    1   ALT-20        87   32.800   0.522    0.071    0.006
    2   ALT-21        88   26.600   0.468    0.073    0.006
    3   MEAN               29.700   0.495    0.072    0.006
    4   %DEV/MEAN          10.440   5.450    1.389    0.000
    5   -----------
    6   BJG-02       138    8.460   0.149    0.013    0.006
    7   BJG-3        139    8.350   0.150    0.011    0.007
    8   MEAN                8.405   0.149    0.012    0.007
    9   %DEV/MEAN           0.650   0.334    8.333    7.690
   10   -----------
   11   ALT-10       188   13.700  10.100    0.185    0.005
   12   ALT-11       189   13.800   9.900    0.206    0.007
   13   MEAN               13.750  10.000    0.196    0.006
   14   %DEV/MEAN           0.364   1.000    5.360   16.670
   15   -----------
   16   BY-20        176    1.770   2.590    0.030    0.000
   17   BY-21        177    1.950   3.000    0.022    0.002
   18   MEAN                1.860   2.795    0.026    0.001
   19   %DEV/MEAN           4.830   7.330   15.380   50.000
   20   -----------
   21   HME-12        79    0.180   2.580    0.456    0.000
   22   HME-13        80    0.135   2.100    0.390    0.000
   23   MEAN                0.158   2.340    0.423    0.000
   24   %DEV/MEAN          13.900  10.256    7.800    0.000
   25   -----------
   26   HME-21       168    6.840   0.162    0.004    0.008
   27   HME-22       169    6.840   0.150    0.004    0.008
   28   MEAN                6.840   0.156    0.004    0.008
   29   %DEV/MEAN           0.000   3.840    0.000    0.000
   30   -----------
------------------------------------------------------------------
```

Data file 22RETEST
Title: REANALYSES OF 22 POND WATERS, W. SAN JOAQUIN VALLEY CA.

Function: PRLIST
Data case no. 1 to 22
Without selection

LIST OF VARIABLES

VAR   TYPE   NAME/DESCRIPTION
  1   text 12   field number
  2   numeric   Lab No.
  3   numeric   B (mg L^-1) / UCR (1+9) DILUTION
  4   numeric   B (mg L^-1) / UCR (1+99) DILUTION
  5   numeric   B (mg L^-1) / CAL.REG.WQCB
  6   numeric   Ca (mg L^-1) / UCR (1+99) DILUTION
  7   numeric   Ca (mg L^-1) / CAL.REG.WQCB

CASE
NO.   1   2   3   4   5   6   7
----
   1   HME-01   68   32.90   42.10   36.00   323.0   310.0
   2   HME-04   71   18.10   21.70   19.00   186.0   180.0
   3   HME-07   74   23.40   26.70   24.00   633.0   620.0
   4   HME-10   77   19.40   22.80   19.00   376.0   370.0
   5   HME-11   78   9.00   10.70   9.10   310.0   360.0
   6   LRG-20   94   20.50   24.80   22.00   61.2   58.0
   7   LRG-23   97   45.00   58.30   48.00   198.0   180.0
   8   LRG-24   98   33.50   45.40   36.00   146.0   130.0
   9   LRG-13   128   74.30   67.70   72.00   190.0   120.0
  10   LRG-14   129   17.20   18.20   16.00   85.6   87.0
  11   LRG-16   131   6.10   7.79   6.40   36.6   44.0
  12   BY-11   158   39.20   51.80   41.00   89.2   87.0
  13   BY-14   161   28.90   25.10   20.00   82.4   70.0
  14   BY-15   162   13.90   17.90   14.00   95.9   69.0
  15   HME-19   166   51.10   71.80   52.00   759.0   610.0
  16   HME-25   172   10.20   13.60   10.00   531.0   450.0
  17   BY-17   173   20.20   24.10   20.00   66.3   58.0
  18   BY-18   174   8.70   10.30   8.70   97.9   86.0
  19   BY-19   175   10.00   12.30   9.80   73.0   71.0
  20   BY-22   178   23.50   27.30   22.00   282.0   320.0
  21   ALT-12   190   64.30   74.40   65.00   71.8   71.0
  22   ALT-16   194   17.30   20.30   16.00   160.0   150.0

Data file 22RETEST
Title: REANALYSES OF 22 POND WATERS, W. SAN JOAQUIN VALLEY CA.

Function: PRLIST
Data case no. 1 to 22
Without selection

LIST OF VARIABLES

VAR   TYPE   NAME/DESCRIPTION
  1   text 12   field number
  2   numeric   Lab No.
  8   numeric   K (mg L^-1) / UCR (1+99)
  9   numeric   K (mg L^-1) / CAL.REG.WQCB
 10   numeric   Mg (mg L^-1_ / UCR (1+99) DILUTION
 11   numeric   Mg (mg L^-1) / CAL.REG.WQCB
 12   numeric   Mo (mg L^-1) / UCR (1+9) DILUTION
 13   numeric   Mo (mg L^-1) / CAL.REG.WQCB

CASE
NO.   1   2   8   9   10   11   12   13
----
   1   HME-01   68   50.1   92.0   1980.0   1900.0   4.31   4.325
   2   HME-04   71   32.9   50.0   1180.0   1100.0   2.79   2.740
   3   HME-07   74   55.6   75.0   2170.0   2200.0   7.06   6.465
   4   HME-10   77   32.1   40.0   611.0   560.0   4.66   4.350
   5   HME-11   78   20.5   21.0   356.0   330.0   2.83   2.600
   6   LRG-20   94   46.8   69.0   931.0   780.0   2.22   2.070
   7   LRG-23   97   93.8   140.0   2060.0   1900.0   4.68   4.535
   8   LRG-24   98   70.5   110.0   1640.0   1400.0   3.53   3.340
   9   LRG-13   128   134.0   260.0   2430.0   2900.0   6.57   5.860
  10   LRG-14   129   42.1   54.0   696.0   630.0   2.53   2.065
  11   LRG-16   131   19.8   26.0   288.0   250.0   1.20   1.080
  12   BY-11   158   69.0   100.0   1490.0   1300.0   3.52   3.120
  13   BY-14   161   37.9   44.0   725.0   600.0   2.26   1.900
  14   BY-15   162   22.5   32.0   496.0   410.0   1.79   1.545
  15   HME-19   166   230.0   280.0   4490.0   4000.0   0.70   0.678
  16   HME-25   172   65.4   73.0   1280.0   1000.0   0.46   0.422
  17   BY-17   173   40.2   48.0   668.0   570.0   2.00   1.670
  18   BY-18   174   17.1   21.0   310.0   270.0   1.22   1.045
  19   BY-19   175   17.8   23.0   350.0   340.0   1.37   1.170
  20   BY-22   178   27.5   26.0   547.0   480.0   2.46   2.100
  21   ALT-12   190   32.5   37.0   168.0   150.0   6.04   5.430
  22   ALT-16   194   23.2   28.0   157.0   140.0   5.29   4.805

Data file 22RETEST
Title: REANALYSES OF 22 POND WATERS, W. SAN JOAQUIN VALLEY CA.

Function: PRLIST
Data case no. 1 to 22
Without selection

LIST OF VARIABLES

VAR	TYPE	NAME/DESCRIPTION
1	text 12	field number
2	numeric	Lab No.
14	numeric	Na (mg L^-1) / UCR (1+99)
15	numeric	Na (mg L^-1) / CAL.REG.WQCB
16	numeric	Si (mg L^-1) / UCR (1+9) DILUTION
17	numeric	Si (mg L^-1) / UCR (1+99) DILUTION
18	numeric	Sr (mg L^-1) / UCR (1+9) DULiTION
19	numeric	Sr (mg L^-1) / UCR (1+99) DILUTION

CASE NO.	1	2	14	15	16	17	18	19
1	HME-01	68	33600.0	30000.0	8.210	9.500	4.63	5.60
2	HME-04	71	17800.0	15000.0	9.410	11.000	3.23	3.60
3	HME-07	74	25500.0	23000.0	0.080	1.700	20.10	21.80
4	HME-10	77	11600.0	10000.0	1.700	3.700	8.60	9.30
5	HME-11	78	5800.0	4900.0	21.400	27.200	6.00	6.40
6	LRG-20	94	13500.0	11000.0	9.100	13.000	0.50	0.56
7	LRG-23	97	27300.0	23000.0	0.220	3.400	2.10	2.60
8	LRG-24	98	21500.0	17000.0	0.280	1.600	1.50	1.90
9	LRG-13	128	35000.0	38000.0	23.400	28.600	1.70	2.24
10	LRG-14	129	10200.0	8500.0	6.200	8.900	0.97	0.82
11	LRG-16	131	4310.0	3400.0	7.000	10.400	0.41	0.33
12	BY-11	158	25100.0	20000.0	3.300	6.300	0.96	1.10
13	BY-14	161	12200.0	9100.0	5.500	10.100	1.02	1.00
14	BY-15	162	8390.0	6400.0	5.000	11.700	1.10	1.40
15	HME-19	166	35600.0	27000.0	3.900	6.100	13.30	17.70
16	HME-25	172	7170.0	5600.0	4.900	10.800	6.00	7.30
17	BY-17	173	11300.0	9000.0	6.600	11.200	0.72	0.63
18	BY-18	174	4970.0	4000.0	12.100	17.600	1.30	1.40
19	BY-19	175	5680.0	4900.0	12.100	17.800	0.92	0.92
20	BY-22	178	11300.0	9600.0	9.900	12.400	6.60	7.10
21	ALT-12	190	21300.0	18000.0	6.600	10.500	6.40	6.40
22	ALT-16	194	9190.0	7400.0	22.300	28.300	5.30	5.40

Data file 22RETEST
Title: REANALYSES OF 22 POND WATERS, W. SAN JOAQUIN VALLEY CA.

Function: PRLIST
Data case no. 1 to 22
Without selection

LIST OF VARIABLES

VAR   TYPE   NAME/DESCRIPTION
  1   text 12   field number
  2   numeric   Lab No.
 20   numeric   U (mg L^-1) / UCR (MARCH 89)
 21   numeric   U (mg L^-1) / UCR (OCTOBER 89)
 22   numeric   U (mg L^-1) / UCR (OCTOBER 89)
 23   numeric   U (mg L^-1) / CAL.REG.WQCB
 24   numeric   V (mg L^-1) / UCR (MARCH 89)
 25   numeric   V (mg L^-1) / UCR (OCTOBER 89)

CASE
NO.   1   2   20   21   22   23   24   25
----
   1   HME-01   68   1.030   1.060   1.050   1.100   0.084   0.066
   2   HME-04   71   0.674   0.690   0.640   0.580   0.139   0.133
   3   HME-07   74   0.241   0.410   0.410   0.460   0.030   0.025
   4   HME-10   77   1.115   0.950   0.950   0.910   0.045   0.043
   5   HME-11   78   1.075   1.250   1.240   1.200   0.100   0.043
   6   LRG-20   94   1.220   1.070   1.060   0.950   0.022   0.025
   7   LRG-23   97   2.420   2.660   2.670   2.500   0.053   0.045
   8   LRG-24   98   1.950   1.840   1.860   1.800   0.051   0.044
   9   LRG-13   128   2.660   2.590   2.670   2.600   0.027   0.017
  10   LRG-14   129   1.020   0.920   0.920   0.810   0.018   0.016
  11   LRG-16   131   0.530   0.500   0.510   0.470   0.042   0.038
  12   BY-11   158   1.340   1.380   1.380   1.300   0.017   0.015
  13   BY-14   161   0.751   0.700   0.700   0.600   0.015   0.011
  14   BY-15   162   0.546   0.550   0.550   0.460   0.012   0.012
  15   HME-19   166   0.269   0.300   0.300   0.290   0.014   0.014
  16   HME-25   172   0.138   0.140   0.150   0.130   0.010   0.010
  17   BY-17   173   0.730   0.700   0.710   0.630   0.030   0.031
  18   BY-18   174   0.496   0.470   0.470   0.370   0.051   0.050
  19   BY-19   175   0.382   0.490   0.480   0.390   0.033   0.035
  20   BY-22   178   0.392   0.450   0.450   0.400   0.040   0.041
  21   ALT-12   190   1.200   1.200   1.200   1.100   0.257   0.257
  22   ALT-16   194   0.460   0.390   0.400   0.360   0.252   0.225

Data file 19-SE-AS
Title: REANALYSIS OF 19 POND WATER SAMPLES, W.SAN JOAQUIN VALLEY CA

Function: PRLIST
Data case no. 1 to 19
Without selection

LIST OF VARIABLES

VAR   TYPE   NAME/DESCRIPTION
 1   text 12   field number
 2   numeric   Lab No.
 3   numeric   Se (ug L^-1) / UCR (RUN 1)
 4   numeric   Se (ug L^-1) / UCR (RUN 2)
 5   numeric   As (ug L^-1) / UCR (RUN1)
 6   numeric   As (ug L^-1) / UCR (RUN 2)

CASE
NO.   1   2   3   4   5   6
----
    1   HME-01   68   5.6   5.1   876.0   847.0
    2   HME-02   69   7.8   8.6   453.0   439.0
    3   HME-03   70   8.6   8.4   255.0   244.0
    4   HME-04   71   7.2   6.9   441.0   428.0
    5   HME-05   72   11.5   10.4   177.0   173.0
    6   HME-06   73   8.9   8.5   25.8   28.1
    7   HME-13   80   39.8   29.6   2250.0   2110.0
    8   LRG-21   95   5.3   6.0   340.0   354.0
    9   LRG-22   96   5.4   8.1   690.0   764.0
   10   EWJ-11   110   0.1   0.1   19.0   27.0
   11   EWJ-12   111   0.1   0.1   54.3   56.4
   12   LRG-10   125   0.5   1.6   127.0   130.0
   13   LRG-11   126   1.3   1.2   248.0   253.0
   14   LRG-13   128   1.5   2.5   381.0   366.0
   15   EWJ-19   134   0.1   0.1   6.6   6.8
   16   EWJ-20   135   0.1   0.1   12.7   14.1
   17   BY-20   176   1.3   1.2   497.0   516.0
   18   ALT-11   189   0.1   0.1   4590.0   4570.0
   19   ALT-14   192   1.9   2.2   532.0   536.0

WQB WITH VALUES MEASURED AT UCR IN DIFFFERENT TIMES
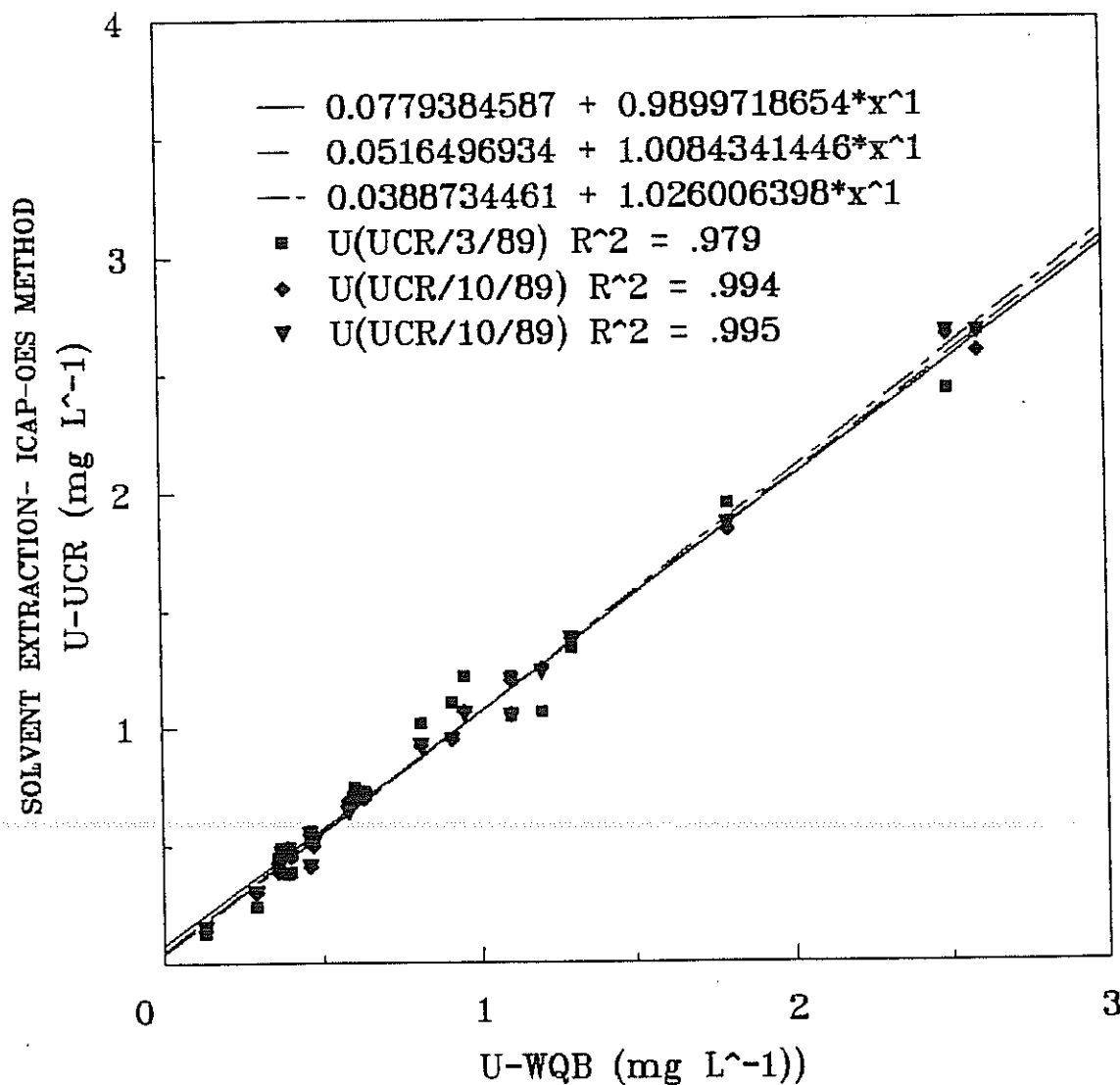
FLUOROMETRIC METHODS, NATURAL RESOURCE LABORATORY, COLORADO

UC3-U-WQ.DT,UC3-U-WQ.GRA, DISK101

COMPARISON OF VANADIUM VALUES

MEASURED IN TWO DIFFERENT RUNS

—— $-0.0023667185 + 1.0075817776*x^1$

$R^2 = .996$

RUN 2 SOLVENT EXTRACTION 10/1989
V-UCR (mg L^-1)

v(10-89)

RUN 1 SOLVENT EXTRACTION 3/1989
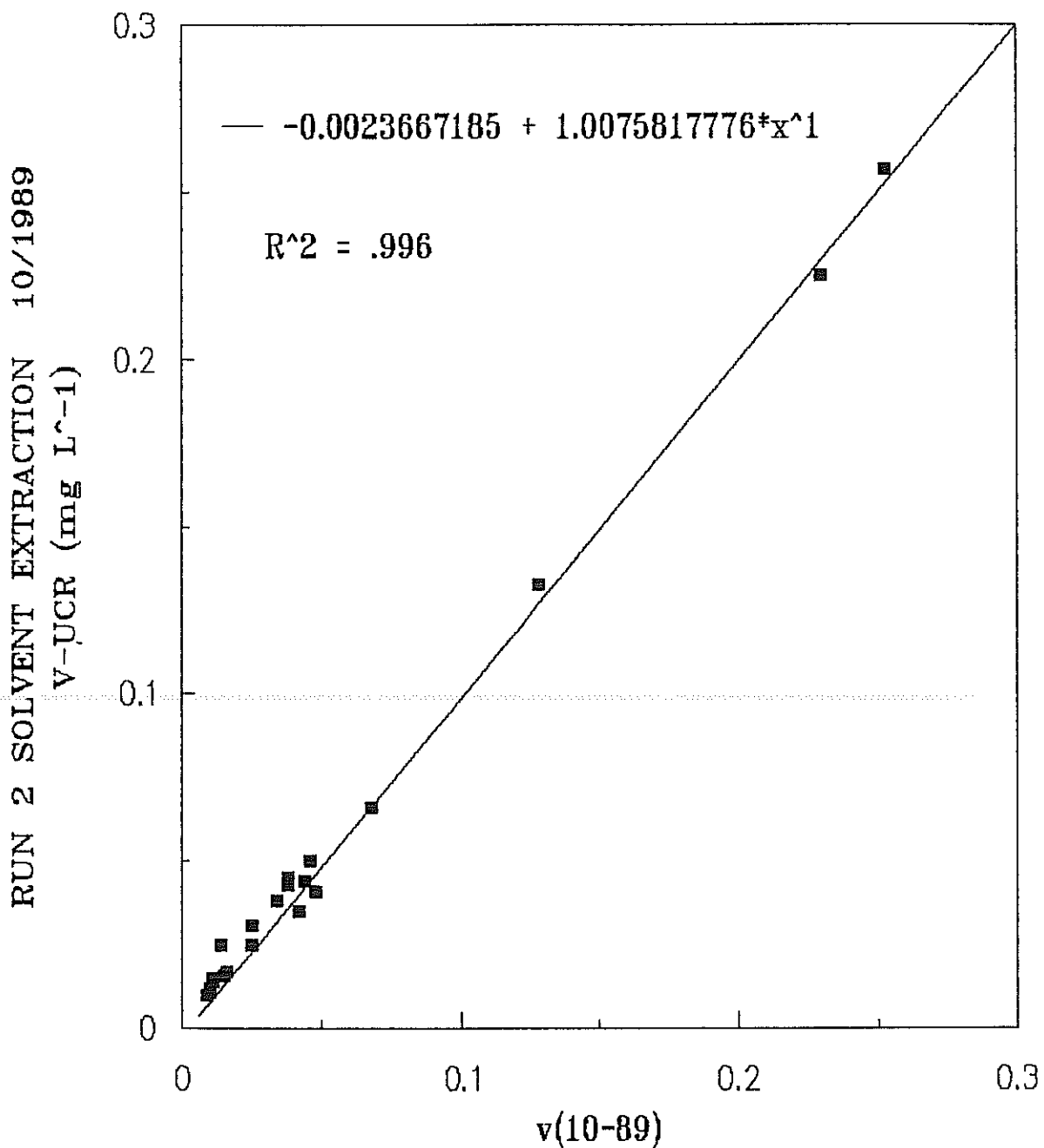
COMPARISON OF CALCIUM VALUES REPORTED BY
WQB AND THOSE MEASURED BY ICAP AT UCR

Plot legend: — $-2.1916748007 + 1.089117273*x^1$

$R^2 = .965$

Y-axis: VALUES MEASURED BY ICAP AT UC RIVERSIDE
Ca-UCR (mg L^{-1})

X-axis: Ca-WQB (mg L^{-1})

VALUES REPORTED BY WATER QUALITY BOARD
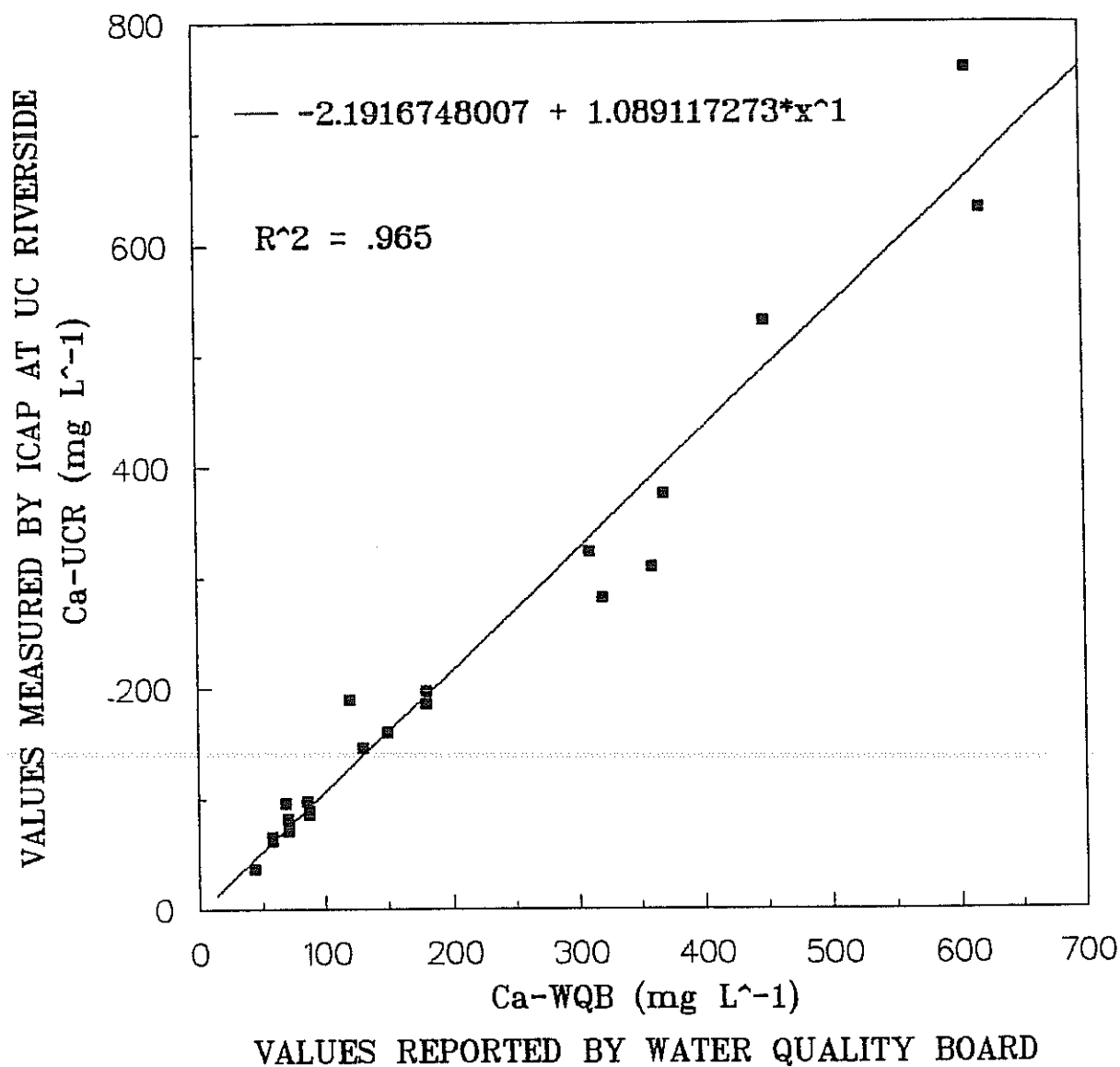
UC-Ca-WQ.DT, UC-Ca-WQ.GRA, DISK101

COMPARISON OF MAGNESIUM VALUES REPORTED BY
WQB AND THOSE MEASURED BY ICAP AT UCR

— $59.475285773 + 1.0217382039*x^1$

$R^2 = .974$

VALUES MEASURED BY ICAP AT UC RIVERSIDE Mg-UCR (mg L^-1)

Mg-WQB (mg L^-1)

VALUES REPORTED BY WATER QUALITY BOARD
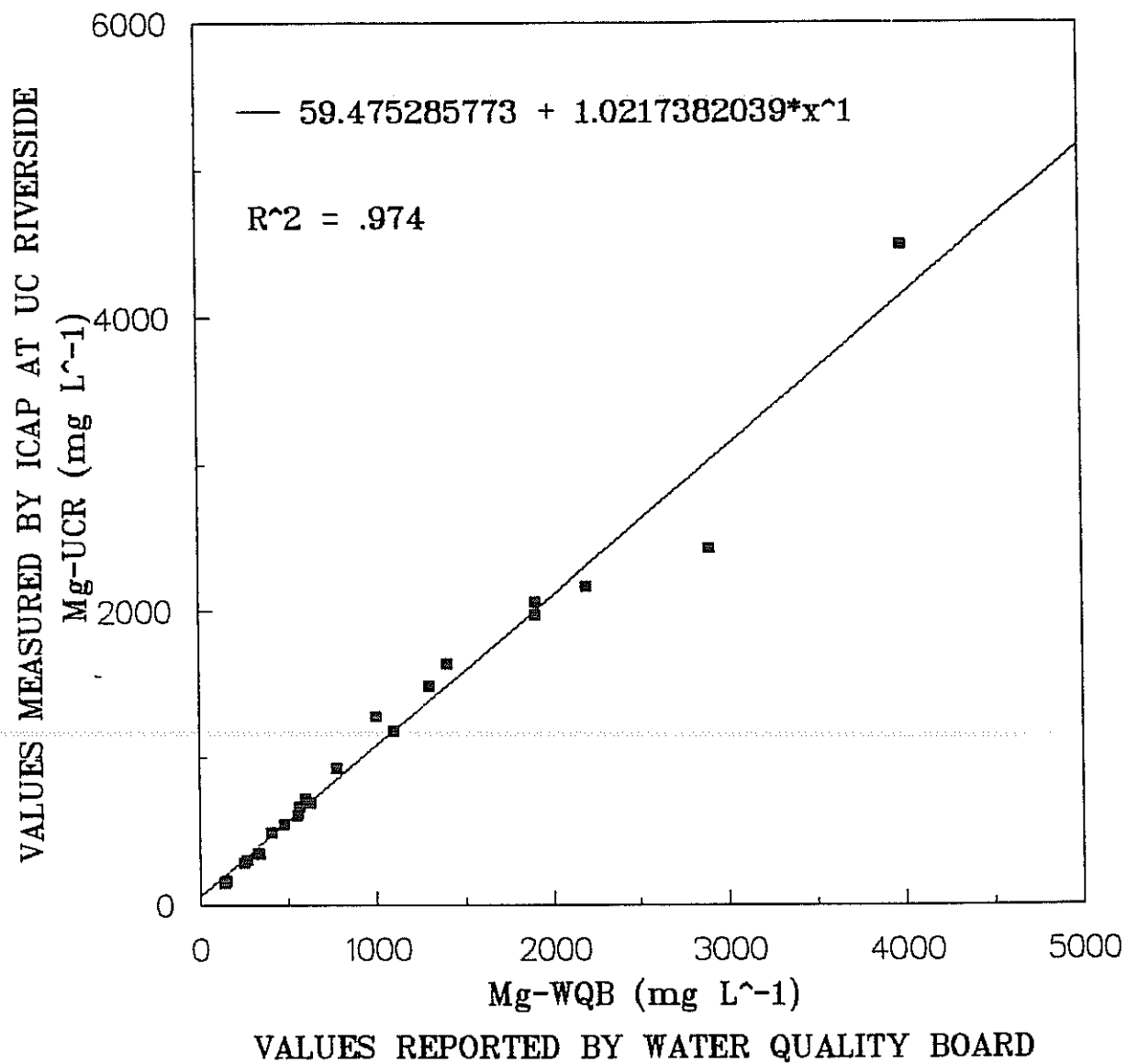
UC-Mg-WQ.DT, UC-Mg-WQ.GRA, DISK101

COMPARISON OF SODIUM VALUES REPORTED BY
WQB AND THOSE MEASURED BY ICAP AT UCR

Plot legend:
— $1743.9065703 + 1.0496852213*x^1$

$R^2 = .957$

Y-axis: VALUES MEASURED BY ICAP AT UC RIVERSIDE Na-UCR (mg L^{-1})

X-axis: Na-WQB (mg L^{-1})

VALUES REPORTED BY WATER QUALITY BOARD
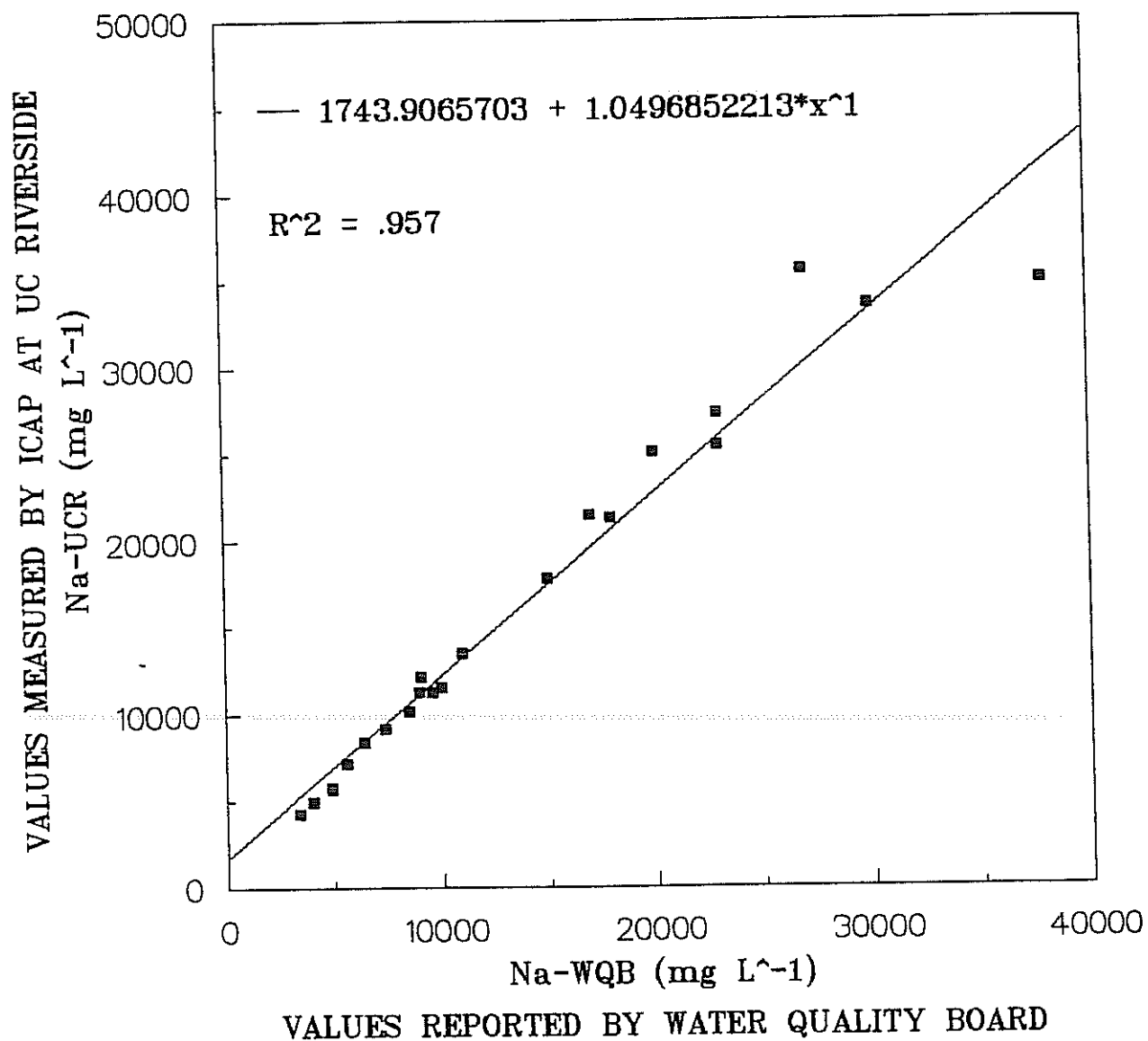
UC-Na-WQ.DT, UC-Na-WQ.GRA, DISK101

WQB AND MEASURED BY ICAP AT UCR

— 4.6142977501 + 0.6548122799*x^1

R^2 = .918

VALUES MEASURED BY ICAP AT UC RIVERSIDE K-UCR (mg L^-1)

K-WQB (mg L^-1)

VALUES REPORTED BY WATER QUALITY BOARD
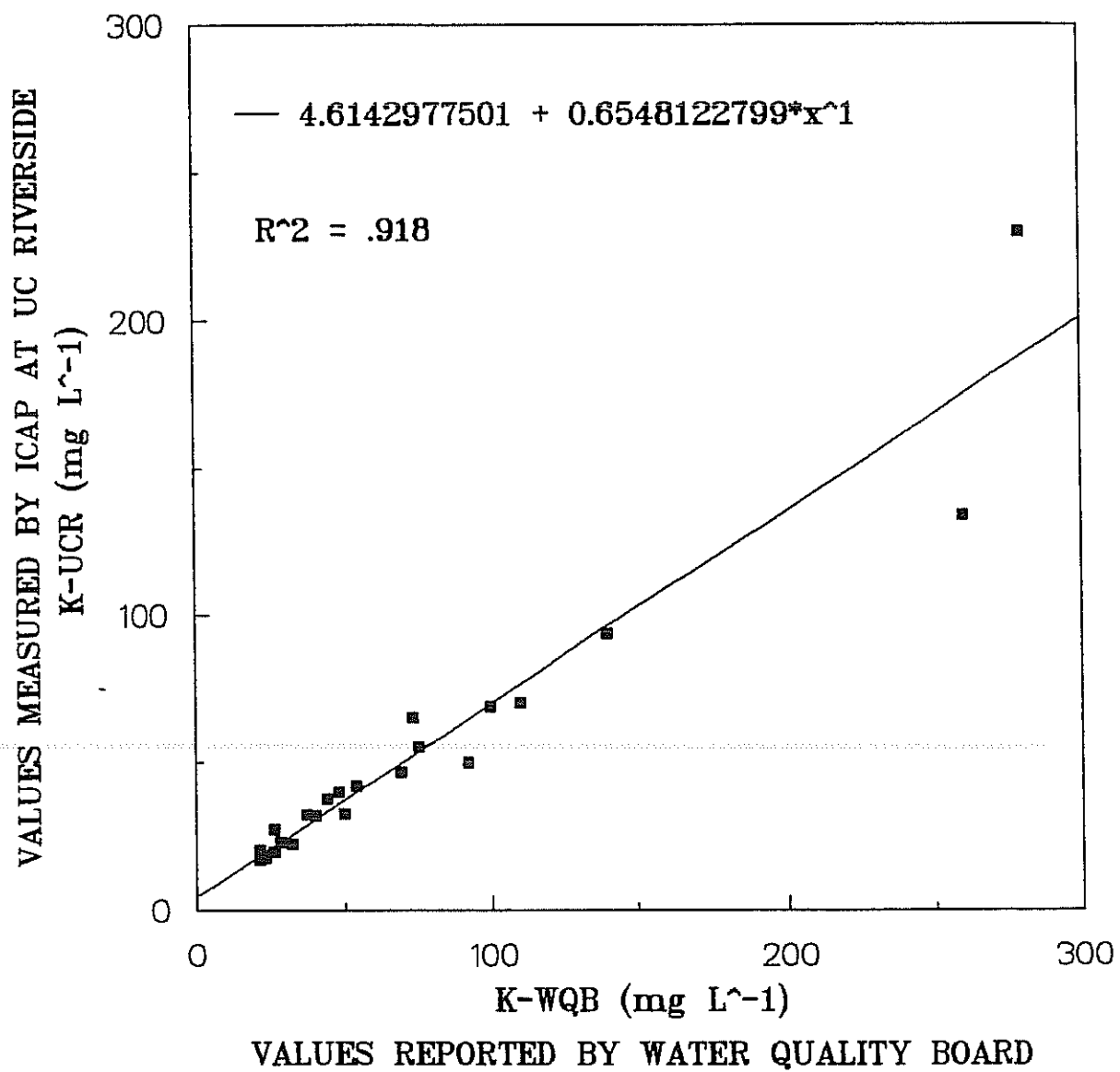
UC-K-WQ.DT, UC-K-WQ.GRA, DISK101

COMPARISON OF BORON VALUES REPORTED BY

WQB AND MEASURED BY ICAP AT UCR

2.2863448058 + 1.100324939*x^1

R^2 = .958

VALUES MEASURED BY ICAP AT UC RIVERSIDE BUCR (mg L^-1)

B-WQB (mg L^-1)

VALUES MEASURED BY WATER QUALITY BOARD

UC-B-WQ.DT, UC-B-WQ.GRA, DISK 101
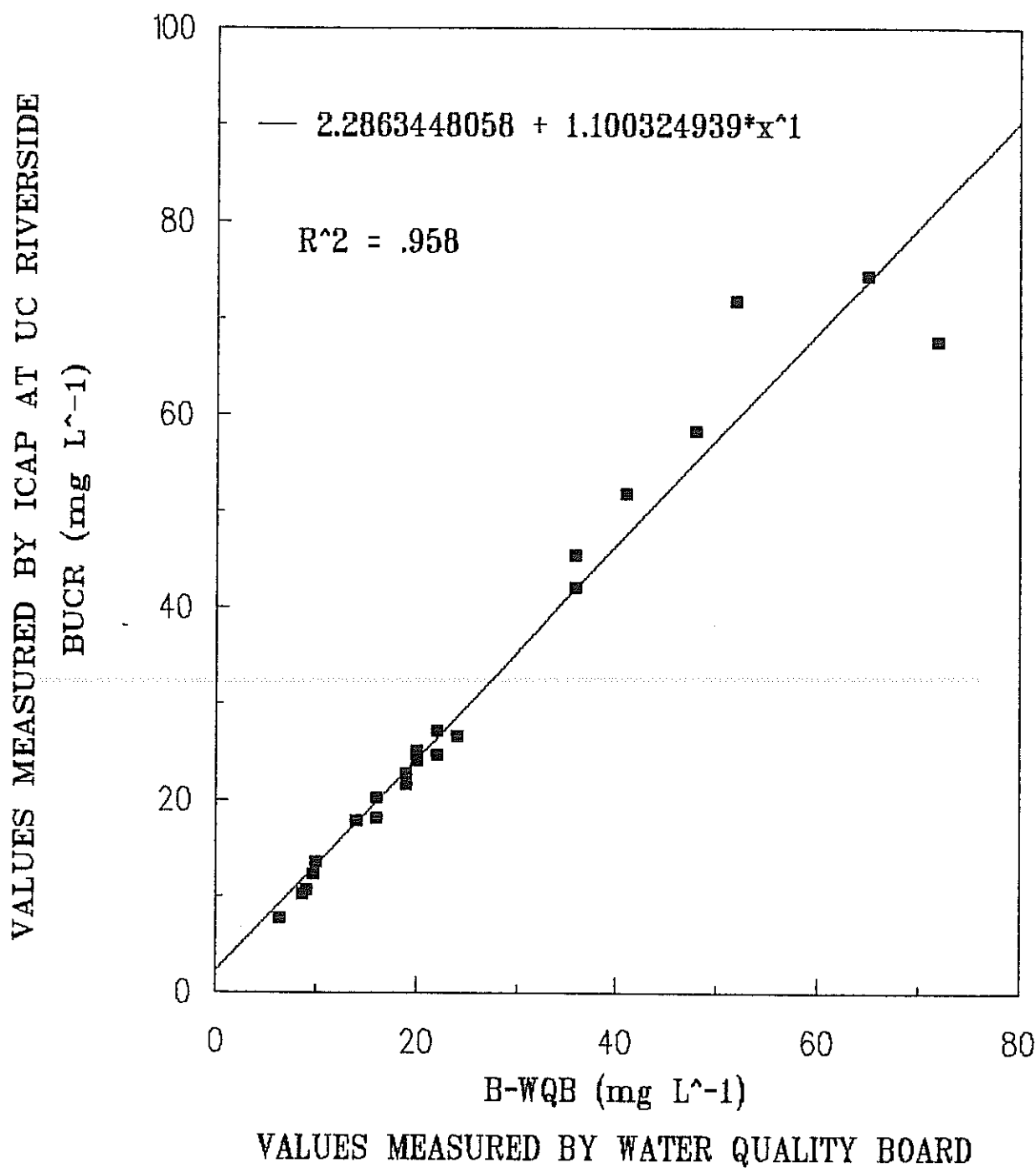
COMPARISON OF SILICON VALUES

MEASURED IN TWO DIFFERENT DILUTIONS
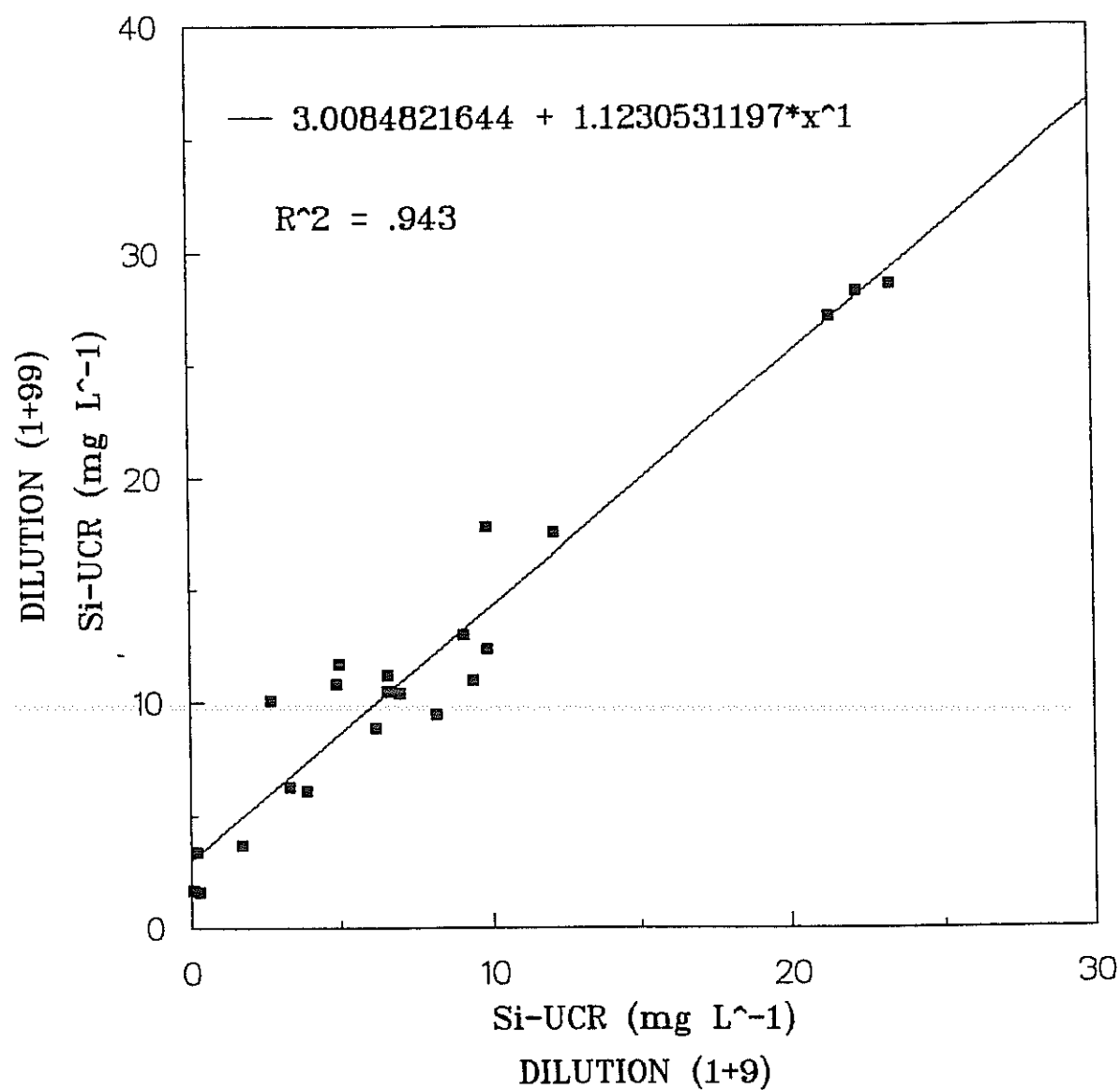
UC-Si-UC.DT, UC-Si-UC.GRA, DISK101

COMPARISON OF STRONTIUM VALUES

MEASURED IN TWO DIFFERENT DILUTIONS

$-0.040134067 + 1.1412030624 * x^1$

$R^2 = .984$

DILUTION (1+99)
SR-UCR (mg L^-1)

Sr-UCR (mg L^-1)
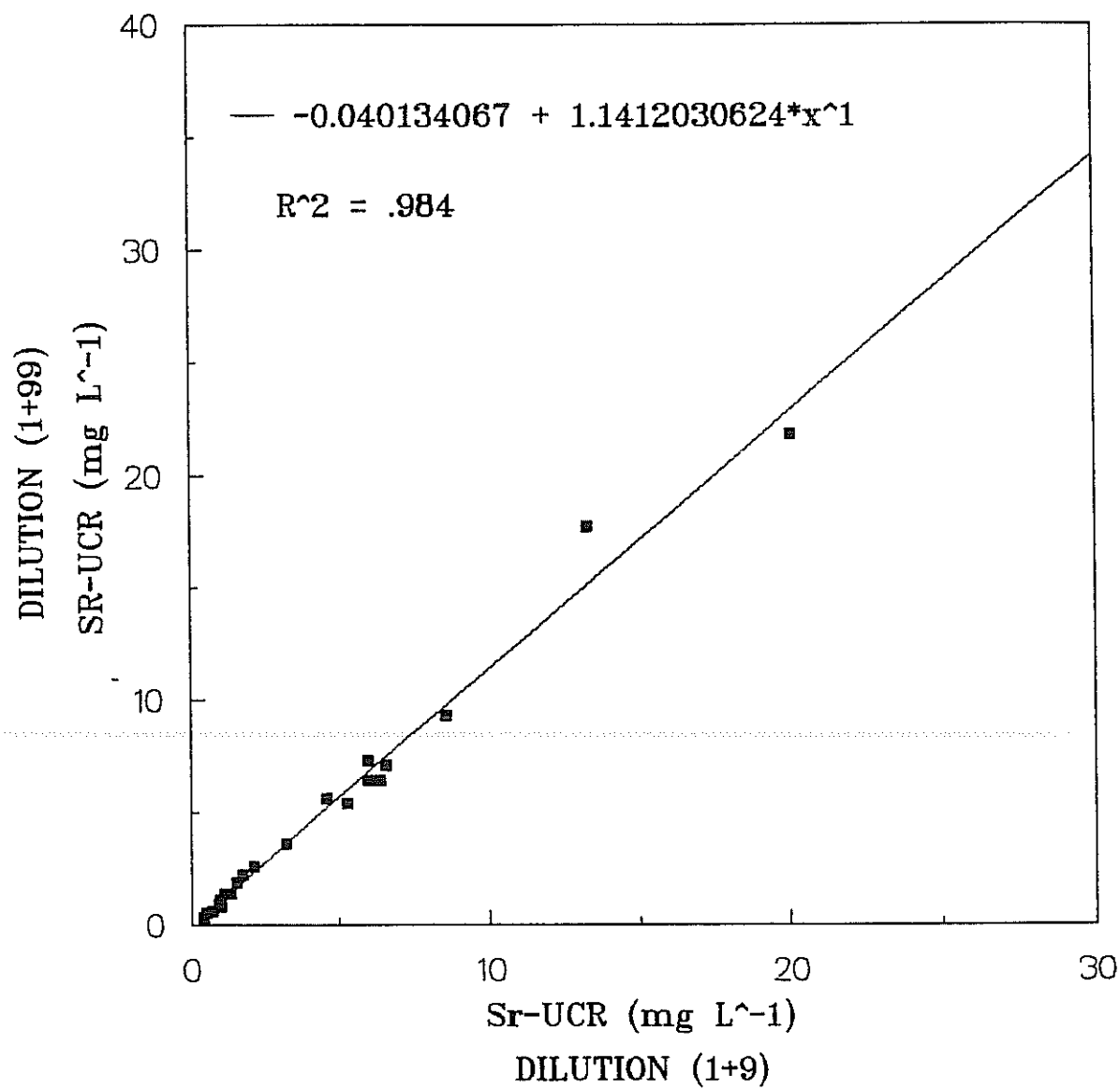
DILUTION (1+9)

UC-SR-UC.DT, UC-SR-UC.GRA, DISK101

COMPARISON OF BORON VALUES

MEASURED IN TWO DIFFERENT DILUTIONS

Plot title: COMPARISON OF BORON VALUES MEASURED IN TWO DIFFERENT DILUTIONS. Y-axis: DILUTION (1+99) B-UCR (mg L^-1). X-axis: B-UCR (mg L^-1) DILUTION (1+9). Legend: 2.2867709314 + 1.0988427467*x^1, R^2 = .926.
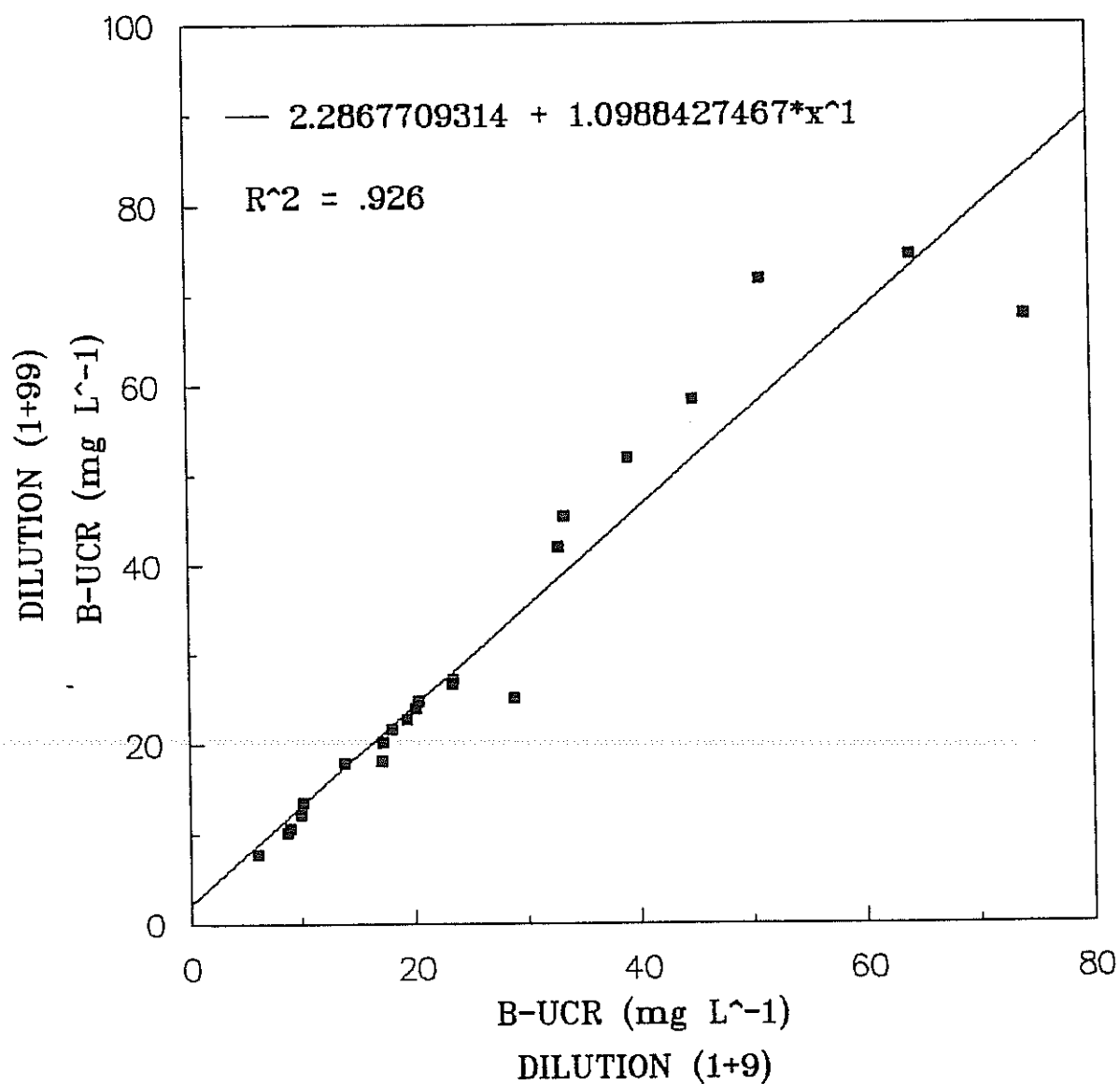
UC-B-UC.DT, UC-B-UC.GRA, DISK101

COMPARISON OF MOLYBDENUM VALUES
MEASURED IN TWO DIFFERENT DILUTIONS

$0.316669982 + 1.209454888 * x^1$

$R^2 = .935$

DILUTION (1+99)
Mo-UCR (mg L^-1)

Mo-UCR (mg L^-1)
DILUTION (1+9)
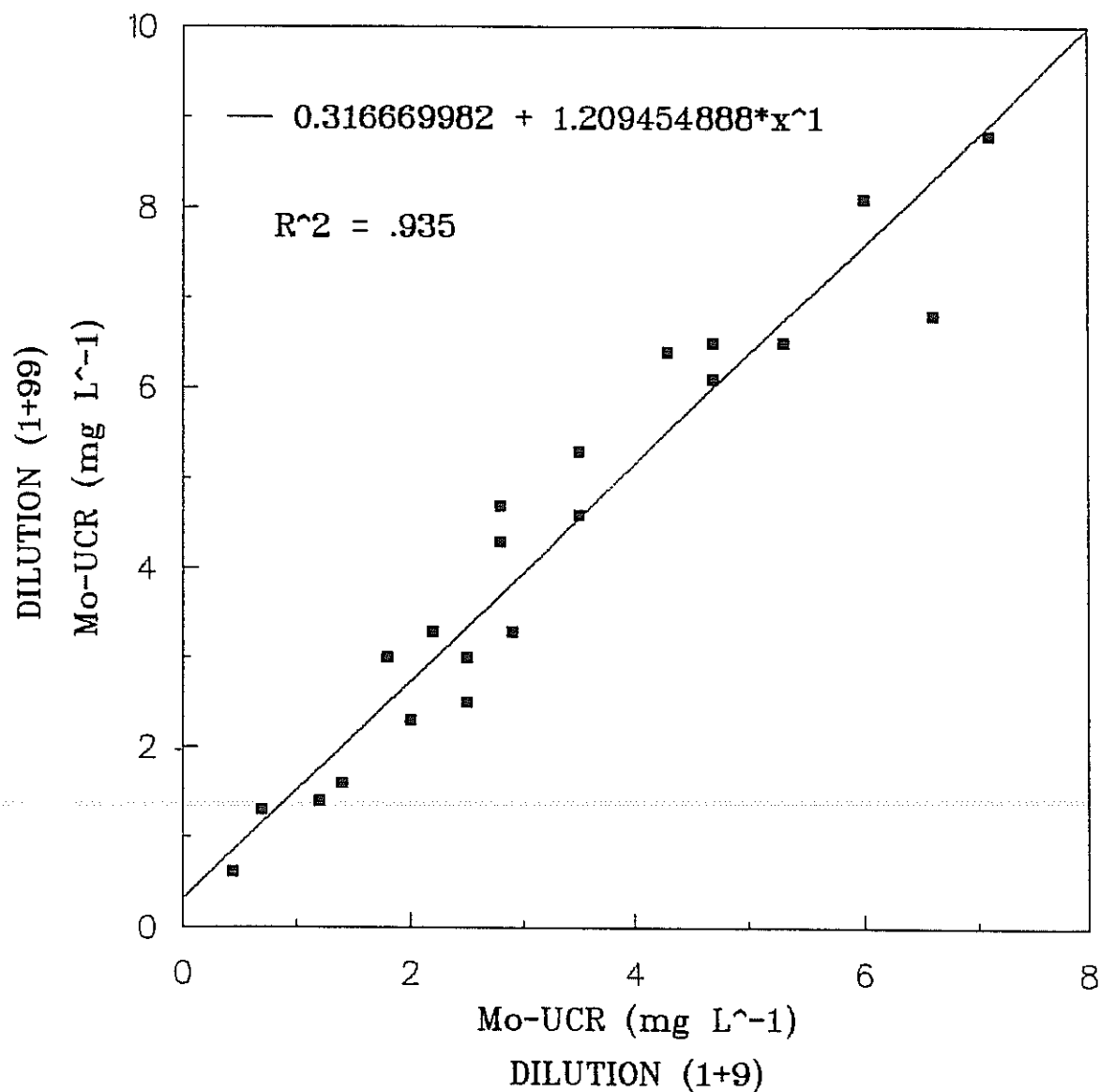
UC-Mo-UC.DT, UC-Mo-UC.GRA, DISK101

COMPARISON OF SELENIUM VALUES

MEASURED IN TWO DIFFERENT RUNS

— 1.0716071364 + 0.7521052749*x^1

R^2 = .972

RUN 2 HYDRIDE GENERATION
Se-UCR (mg M^-3)

Se-UCR (mg M^-3)

RUN 1 HYDRIDE GENERATION
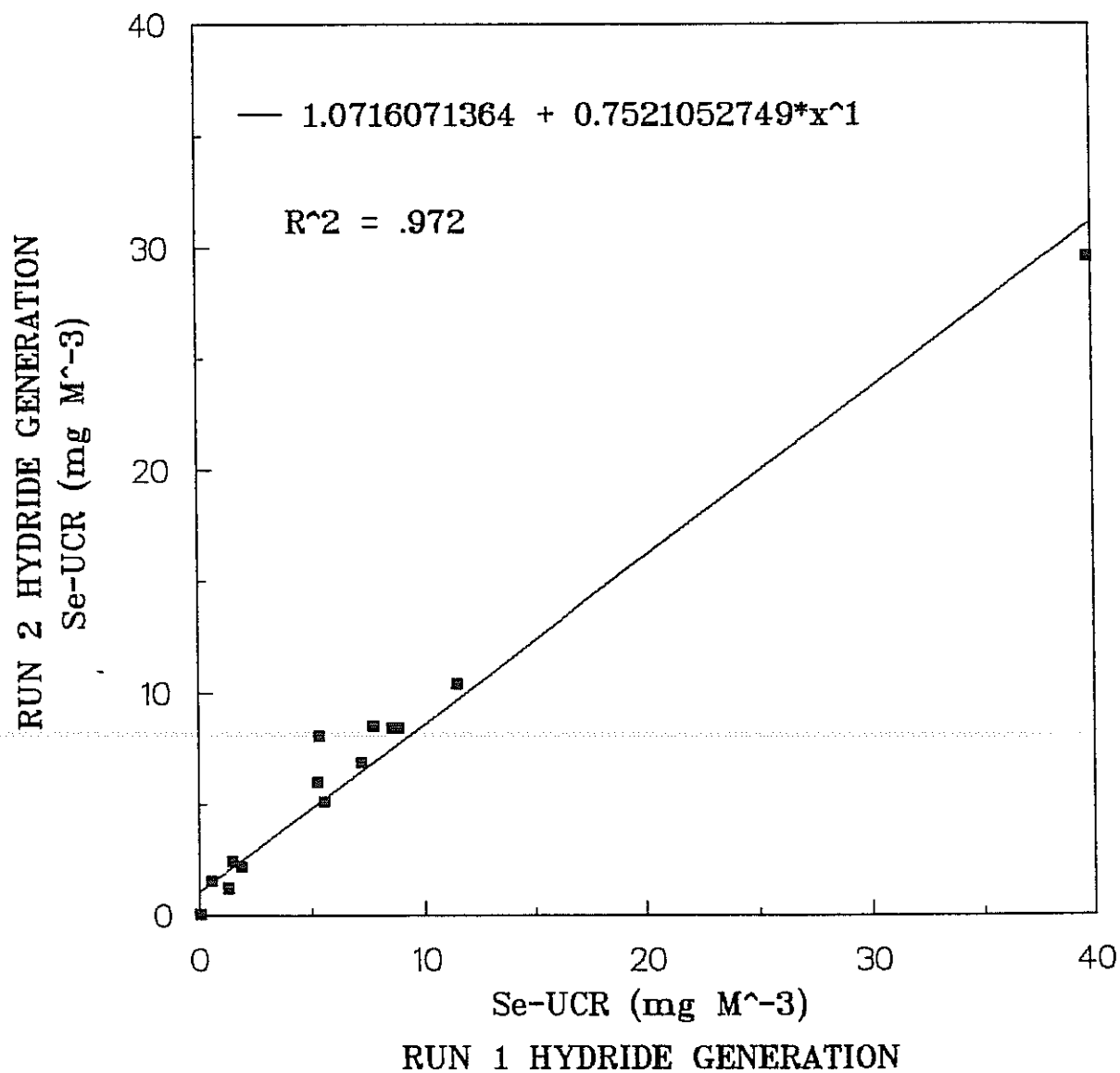
UC-Se-UC.DT, UC-Se-UC.GRA, DISK101

COMPARISON OF SELENITE VALUES

MEASURED IN EXTRACTS AT DIFFERENT TIMES

— $-0.0028278689 + 0.968852459*x^1$

Y-axis: RUN 2 SOLVENT EXTRACTION Se^+4(mg L^-1)

X-axis: Se^+4 (mg L^-1)

RUN 1 SOLVENT EXTRACTION
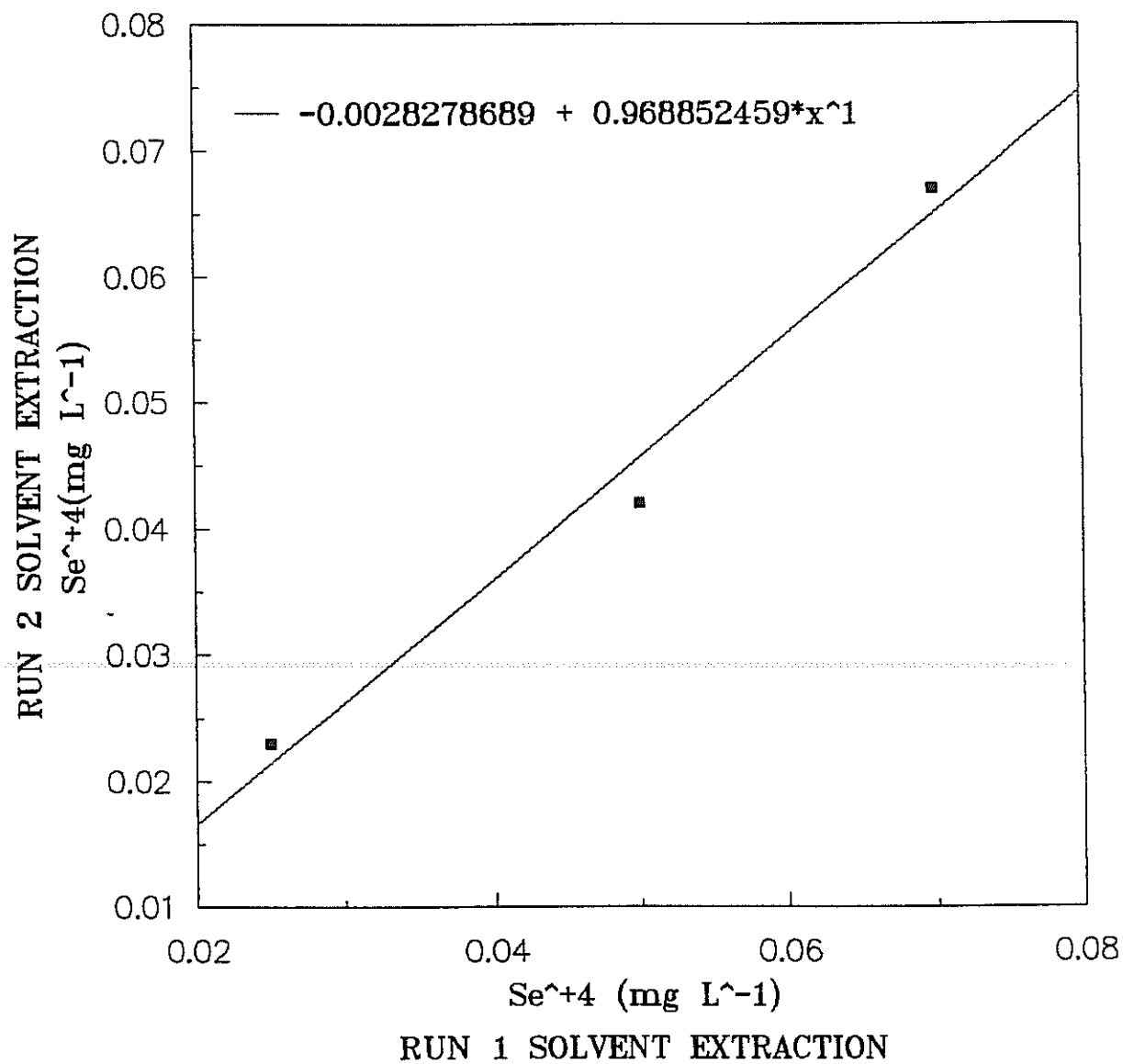
Se4-Se4.DT, Se4-SE4.GRA, DISK101

SELENITE MEASURED BY SOLVENT EXTRACTION
VS. TOTAL SELENIUM BY HYDRIDE GENERATION
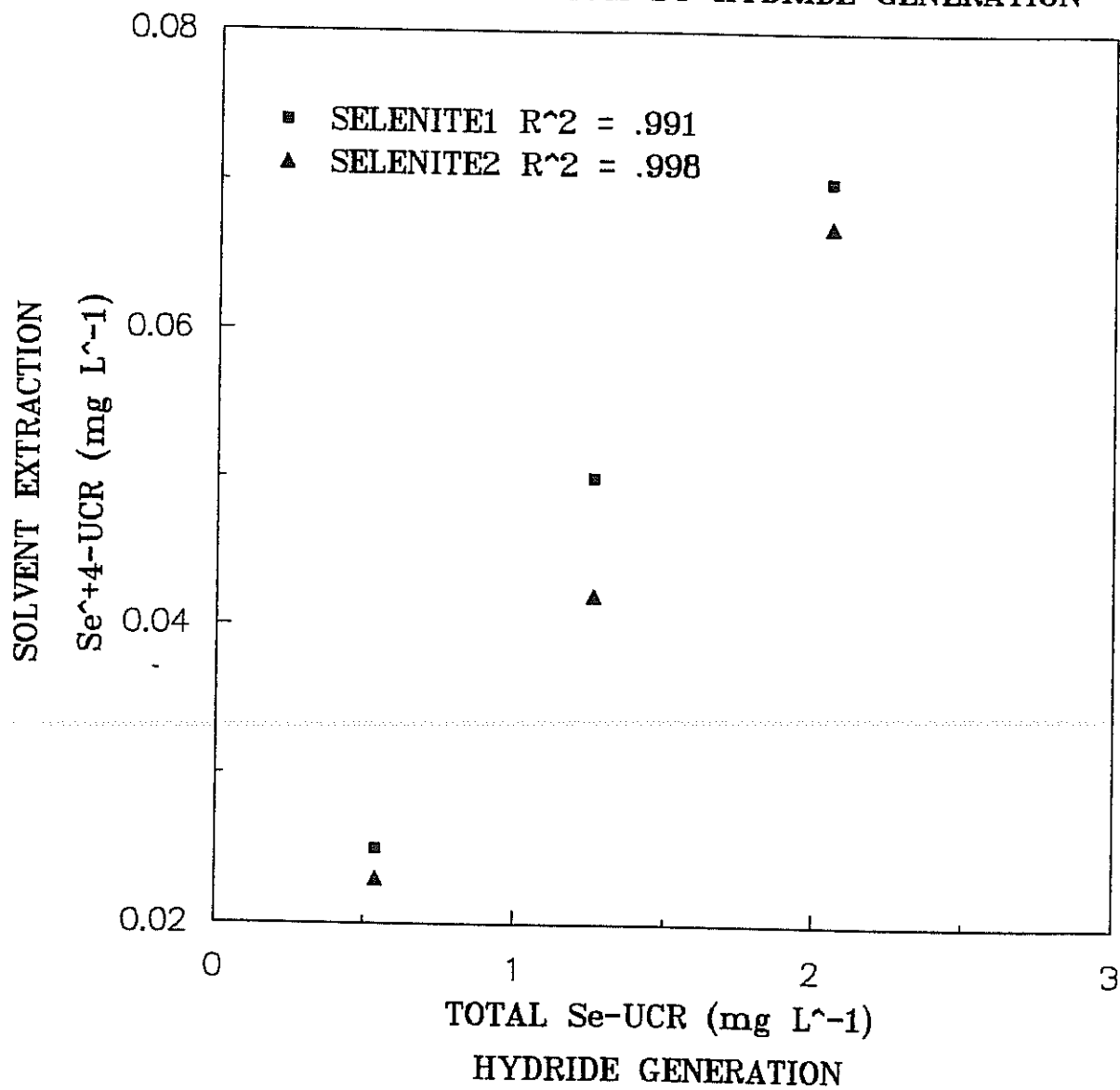
SELENITE.DT, SELENITE.GRA, DISK101

COMPARISON OF ARSENIC VALUES
MEASURED IN TWO DIFFFERENT RUNS

— $3.3583876577 + 0.9852356192*x^1$

$R^2 = .999$

RUN 2 HYDRIDE GENERATION
As-UCR (mg M^-3)

As-UCR (mg M^-3)

RUN 1 HYDRIDE GENERATION
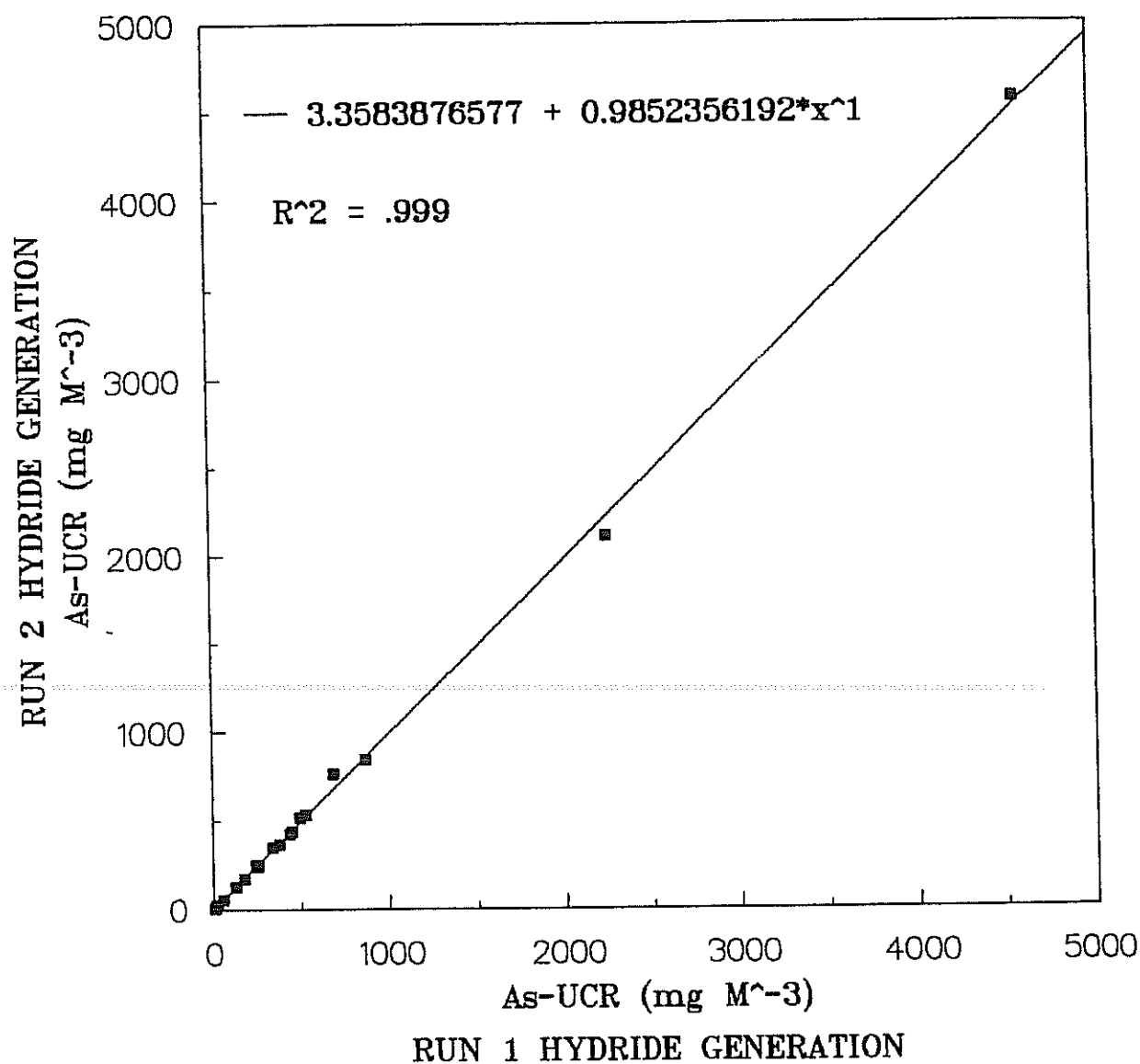
UC-As-UC.DT, UC-As-UC.GRA, DISK101

COMPARISON OF URANIUM VALUES REPORTED BY

WQB AND THOSE MEASURED BY ICAP AT UCR

$$ 0.0498823651 + 0.9150439967 * x^1 $$

$$ R^2 = .937 $$

Y-axis: SOLVENT EXTRACTION - ICAP-OES METHOD U-UCR (mg L^-1)

X-axis: U-WQB (mg L^-1)
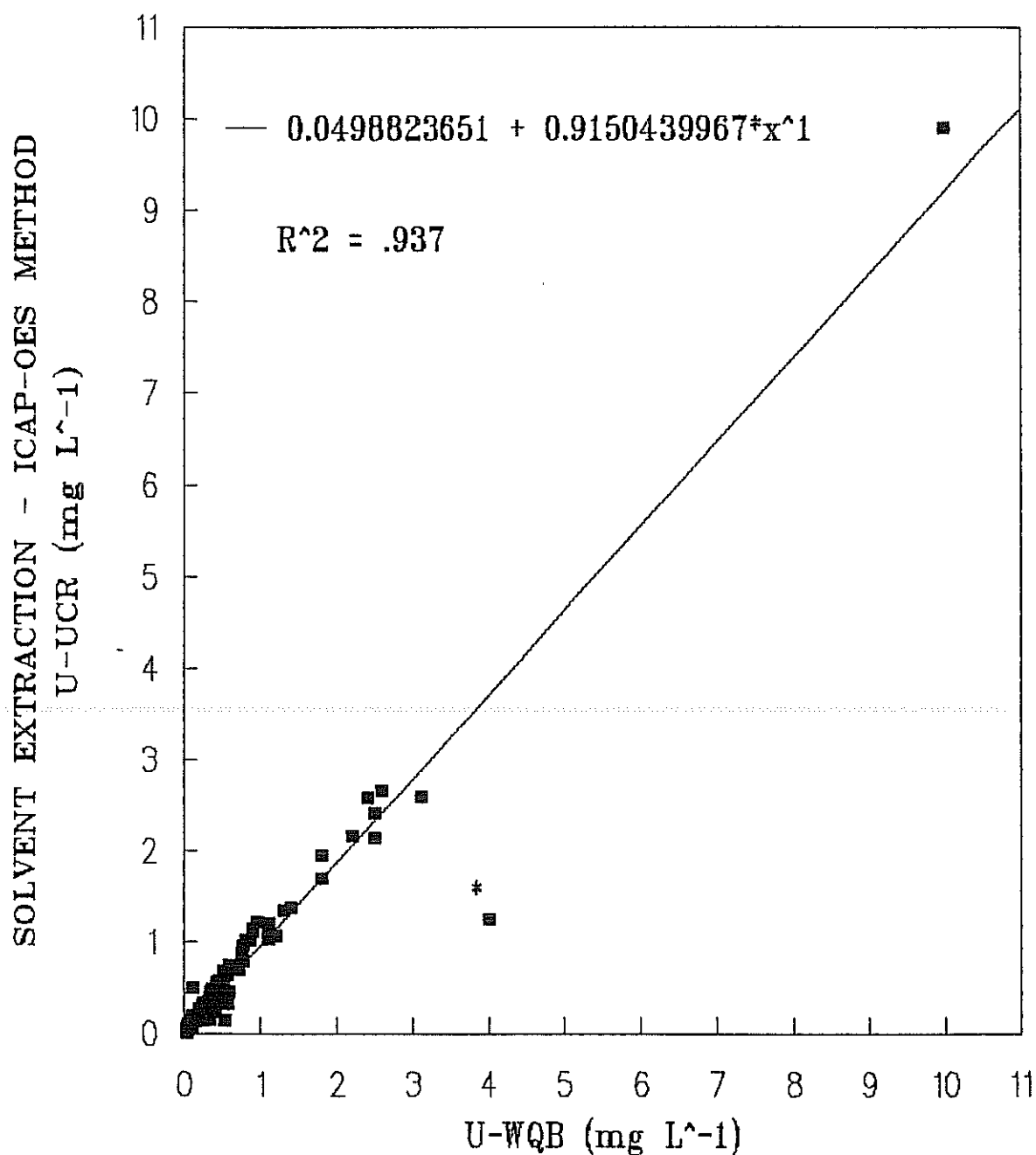
*UCR value for ALT-0-9 reconfirmed by reanalyses

COMPARISON OF MOLYBDENUM VALUES MEASURED BY
WQB AND THOSE MEASURED BY ICAP AT UCR
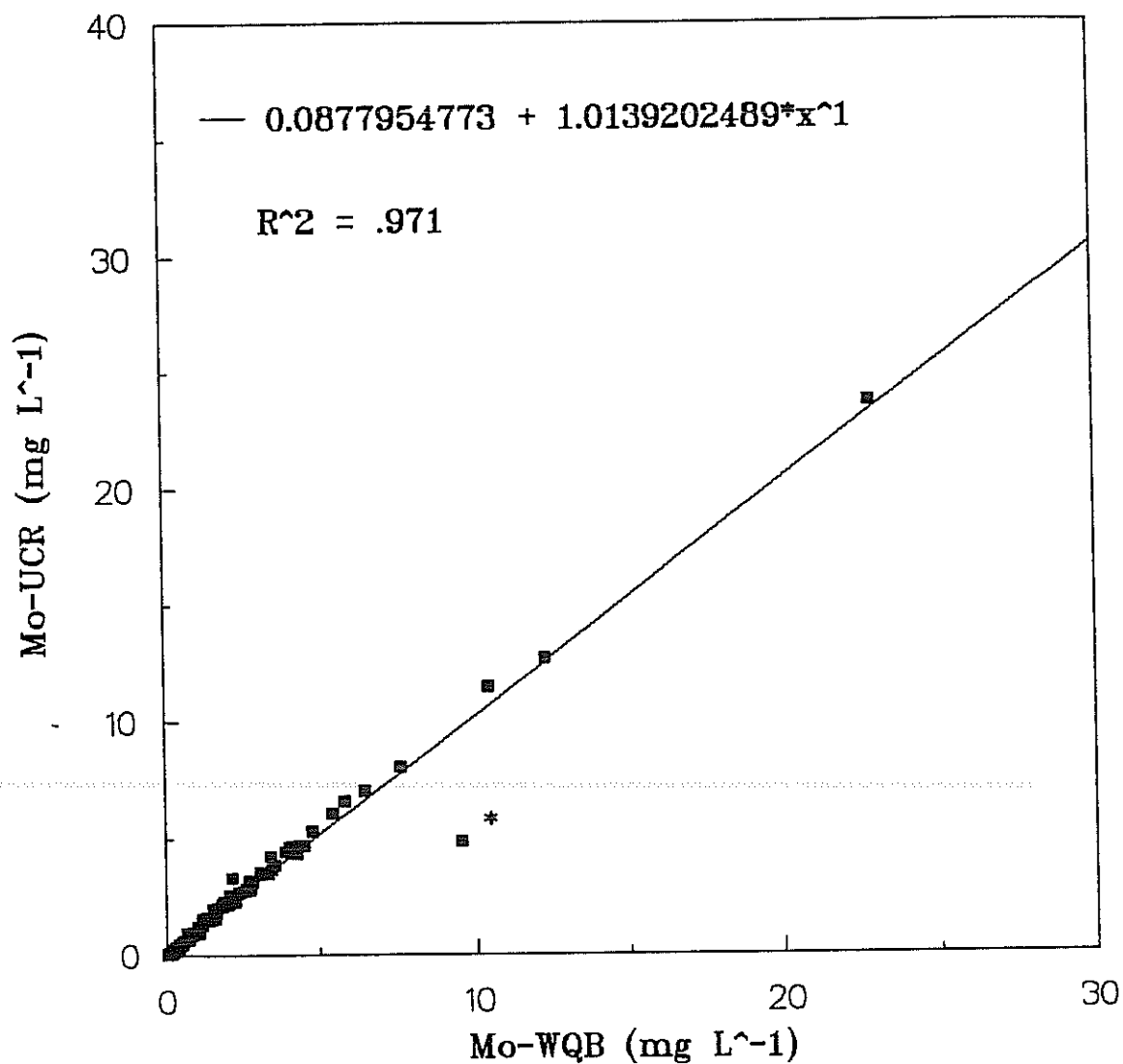
*UCR value for ALT-0-9 reconfirmed by reanalyses

UC-Mo-WQ.DT, UC-MO-WQ.GRA, DISK101

APPENDIX D

SEDIMENT METHOD

Dissolution of Soils and Geological Materials for Simultaneous Elemental Analysis by Inductively Coupled Plasma Optical Emission Spectrometry and Atomic Absorption Spectrometry

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A method has been developed using hydrogen peroxide, 6 M HCl and dilute HF for the dissolution of soils and geological materials. Boron, Si, Se, As and other elements often volatilised by other methods were retained by using closed containers at relatively low temperatures and by avoiding the use of perchloric acid. Six United States Geological Survey (USGS) standard rock samples and additional soil and sediment samples were dissolved and analysed by simultaneous multi-element inductively coupled plasma optical emission spectrometry to test the effectiveness of the method. The results compared favourably with other methods used for the analysis of USGS standards. Analyses of soil and sediment samples indicated that Se and As were retained and measured accurately.

Keywords: *Acid dissolution; volatilisation; multi-element analysis; inductively coupled plasma optical emission spectrometry; atomic absorption spectrometry*

A method for the complete dissolution of soils and geological materials which minimises losses of volatile constituents and contamination from reactants should be of interest to those engaged in agricultural, geological and related environmental research. Analysis of the resulting solutions by inductively coupled argon plasma optical emission spectrometry (ICP-OES) offers the advantages of fast, simultaneous, multi-element analysis.

Minerals. rocks and soil samples can be decomposed chemically by fusion and/or dissolution in acids. Decomposition by fusion is relatively rapid; however, there are some disadvantages. (1) Samples cannot be analysed for elements comprising the added flux. This may include Li, B, Ba. Na. K, S, F, etc., depending on the choice of flux. These elements are often of particular interest in environmental studies and in soil genesis and classification, especially in arid regions of the world. (2) Some elements such as Se. As. Sb and Hg[1] may be partially lost by volatilisation during fusion, while compounds such as CaF_2 may be precipitated during acid dissolution of the fusion residue. (3) High concentrations of the elements comprising the flux often cause matrix problems in the final analyses.

The dissolution of rocks and minerals in acids is a relatively successful process when the type and concentration of acid(s), the temperature and the duration of heating and agitation have been optimised. Hydrogen haloacids, sulphuric acid (H_2SO_4), perchloric acid ($HClO_4$), orthophosphoric acid (H_3PO_4), nitric acid (HNO_3) and some organic acids have been used individually or in combination in dissolution processes.

Although there are conflicting reports in the literature, we conclude, both from our own experience and from the work of others, that if volatile elements are to be determined the use of high boiling-point acids such as $HClO_4$ and H_2SO_4 should be avoided and hydrofluoric acid (HF) should be used only in a specified sequence and dilution.

Langmyhr and Sveen[2] state that Berzelius was the first to use a mixture of HF and H_2SO_4 as a decomposing agent for rock samples. After the dissolving reactions were complete, excess of HF had to be removed by evaporation. Silicon was lost during this operation and had, therefore, to be determined using a separate sample. Hillebrand[3] experienced difficulties in completely removing HF by evaporation and advised against its use as a decomposing agent. Case[4] used HF, in addition to other common mineral acids, to increase the rate of dissolution of certain non-ferrous alloys and silicon

was finally determined spectrophotometrically as yellow silicomolybdic acid. Case[4] used boric acid to complex the excess of HF. Odegard[5] digested rock samples with 40% HF and later added 4.5% H_3BO_3 solution to complex free HF and introduce B as a reference element.

A survey of the extensive literature on the analysis of rocks and minerals showed that HF is often applied in combination with other acids when used as a decomposing agent. However, some rock-forming minerals are very resistant to dissolution when treated with mixtures of HF and H_2SO_4, HNO_3, and/or $HClO_4$. Langmyhr and Sveen[2] investigated the ease with which 28 major and some trace minerals of silicate rocks could be decomposed with a mixture of HF and $HClO_4$. After 20 min of treatment with the acid mixture, quartz (SiO_2), enstatite ($MgSiO_3$), anthophyllite [$(Mg,Fe)_7Si_8O_{22}(OH)_2$], beryl ($Be_3Al_2Si_6O_{18}$), kyanite ($Al_2SiO_5$), topaz [$Al_2SiO_4(F,OH)_2$], staurolite [$Fe(OH)_2Al_4O_2Si_2O_8$], andradite [$Ca_3Fe_2(SiO_4)_3$], epidote [$Ca_2(Al,Fe)_3(SiO_4)_3(OH)$], magnetite ($Fe_3O_4$), pyrite ($FeS_2$), chalcopyrite ($CuFeS_2$) and pyrrhotite ($Fe_{1-n}S$) were only partially decomposed. When the reaction time was increased to 40 and then 60 min, beryl, kyanite. topaz, staurolite. pyrite, chalcopyrite and pyrrhotite were still only partially decomposed. With the exception of topaz, these minerals were found to decompose completely at higher temperatures in bombs lined with fluorinated ethylene-propylene resin (FEP). Langmyhr and Sveen also indicated that HF alone was more effective as a decomposing agent than a mixture of HF with another mineral acid. Antweiler[6] reported that the rate of reaction of silicates with HF was slowed down by the addition of another mineral acid. Dolezal *et al.*[7] reviewed the techniques used for the decomposition of rocks and minerals with mineral acids for analytical purposes. They stated that "according to current opinions, addition of mineral acid hinders the hydrolysis of silicon fluoride, binds the reaction water and causes a shift of equilibrium, leading to a complete decomposition of the rock."

Dolezal *et al.*[7] also studied the volatilisation of the fluoride forms of some elements during decomposition with HF. They concluded that decomposition with HF was not suitable for the determination of As in ores, shale or silicates. In a study of the volatilisation of Se tracers, Chau and Riley[8] spiked portions of marine sediments with ^{75}Se and left them to digest overnight in a water-bath with 1 + 1 HNO_3 - HF. Excess of HF was evaporated in the presence of HNO_3 under an infrared heater and the residue was dissolved in 4 M HCl, boiled to reduce Se^{VI} to Se^{IV}, diluted and then counted for the ^{75}Se activity

Table 1. Wavelengths for ICP-OES and calculated instrumental detection limits

Element	Wavelength/nm	Calculated detection limit*/mg l⁻¹
Aluminium	308.21	0.03
Arsenic	193.69	0.001†
Antimony	206.83	0.001†
Barium	493.40	0.002
Beryllium	234.86	0.0005
Boron	249.67 II‡	0.005
Bismuth	223.06 II	0.001†
Cadmium	228.80 II	0.004
Calcium	393.36	0.005
Calcium	317.80	0.050
Chromium	267.71	0.002
Cobalt	228.61	0.005
Copper	324.75	0.010
Gold	242.80	0.005
Germanium	199.82	0.001†
Iron	259.94	0.005
Lead	220.35	0.020
Lithium	670.70	0.005
Magnesium	279.55	0.020
Manganese	257.61	0.005
Mercury	253.65	0.001†
Molybdenum	202.03 II	0.008
Nickel	231.60	0.010
Potassium	766.40	1.0
Phosphorus	214.90	0.050
Selenium	196.02	0.001†
Scandium	341.38	0.001
Silicon	251.61	0.010
Silver	328.06	0.005
Sodium	588.90	0.20
Strontium	421.50	0.008
Tellurium	214.20 II	0.001†
Thallium	190.86 II	0.100
Tin	284.00	0.100
Titanium	334.90	0.010
Uranium	385.96	0.20
Vanadium	292.40	0.010
Zinc	206.20 II	0.005

* Detection limits vary with the sample matrix.

† Continuous hydride system with ICP-OES.

‡ II = second-order lines.

the fluorides of Ca, Mg, Ba and Sr. Because the solution is dilute, the compounds will tend to form a sol, which dissolves readily when agitated or shaken.

Experimental

In order to develop and test the proposed dissolution method, six United States Geological Survey (USGS) reference samples,[17] a sample of colemanite ($Ca_2B_6O_{11}.5H_2O$) and a sample of pure quartz were decomposed and analysed for mineral elements as follows.

Quadruplicate samples of each material were weighed in FEP centrifuge tubes and, except for quartz, treated with H_2O_2 and HCl according to steps 1–4 of the procedure described under Dissolution. Colemanite dissolved completely in 6 M HCl. The residues from the reference and quartz samples were decomposed with HF according to steps 5 and 6 of the dissolution procedure. The HCl and HF digests were each made up to 100 ml with 6 M HCl and then diluted further prior to analysis by ICP-OES. Aqueous solutions were analysed using a pneumatic nebulisation technique. A Jarrell-Ash Atomcomp Series 800 ICP spectrometer was used; however, atomic absorption spectrometry (AAS) and/or other instrumentation and analytical methods can be used in the final analyses. For system operation the argon flow-rates were as follows: coolant, 14 l min⁻¹; and sample, 0.5 ml min⁻¹. The remaining parameters were the following: plasma, 0 l min⁻¹;

argon pressure to nebuliser, 345 kPa; observation height, 13 mm above the coil; incident power, 1.25 kW; reflected power, <10 W; nebuliser type, cross-flow; integration time, 17 s on-line, 17 s background; and sample aspiration rate, 2.5 ml min⁻¹ via a peristaltic pump. Analytical lines (nm) and approximate detection limits are shown in Table 1.

The USGS standards were analysed for Se and As, but these elements were not positively identified. In order to test and confirm the validity of the proposed dissolution method for the analysis of soils and geological materials for Se and As, two different approaches were used. First, four standard sediment samples, prepared by the US Bureau of Reclamation, were digested and analysed. The samples were distributed to several laboratories to assess the accuracy of different analytical techniques for the measurement of Se in sediments of the San Joaquin Valley, California, USA. Second, known amounts of Se and As were added to a soil sample, a rock sample and a sediment sample and the blanks and spiked samples were digested and then analysed by ICP-OES.[18]

The dissolution technique described below has been tried and tested extensively. Its effectiveness in retaining volatile elements is due to the fact that violent chemical reactions at high temperatures are avoided. An alternative and more rapid dissolution procedure for soils high in organic matter, where elements such as Se are mainly concentrated, has been developed by the authors using concentrated HNO_3 in closed containers and will be the subject of a future paper.

We encountered a number of problems when working with samples that had been processed to a very fine particle size so that they passed through a 200-mesh sieve (0.074 mm). A fine dust was produced and moisture was absorbed during the sieving, weighing and other handling operations. Very fine particle size samples formed dense, moist lumps similar to clay balls, which were difficult to disperse and dissolve in H_2O_2 or acids. Langmyhr and Sveen[2] encountered similar problems during a study of the effect of particle size on HF dissolution. Antweiler[6] recommended the use of HF for the decomposition of silicate fragments that had been neither crushed nor ground. Other disadvantages of preparing fine particle size samples are the increased time required for sample preparation and the increased potential for contamination by metals from steel ball mills and other metallic grinding apparatus. Pulverisation may be necessary, however, for samples to be brought into solution by fusion, especially for minerals such as chromite and zircon and others that are resistant to acid dissolution. With USGS samples containing chromite, fine grinding did not prevent incomplete acid dissolution.

Dissolution Technique

Equipment

Quartz mortar and pestle.
Plastic 60-mesh (<0.25 mm) sieve or screen.
Digestion block adjustable to 90 °C or sand-bath.
Oak Ridge FEP centrifuge tubes (50 ml) with sealing caps.
Reciprocal two-speed shaker.
High-speed centrifuge with rotor that holds 50-ml Oak Ridge centrifuge tubes.
Plastic calibrated containers (100 ml).
FEP pipettes or plastic-tip dispensers.

Reagents

Hydrogen peroxide, 30%.
Hydrochloric acid, concentrated (38%) and 1 + 1.
Hydrofluoric acid, 49%.
De-ionised, distilled water (DDW).

Dissolution

Crush a 50-g sample of air-dried soil or rock into small pieces using a non-metallic tool. For further grinding, use a quartz

Table 3. Concentration of mineral elements in USGS standard rock sample G-2. The UCR columns represent values obtained using H_2O_2 - HCl - HF dissolution and analysis by ICP-OES. The USGS column represents the range of values reported by Flanagan.[17] The Abbey column represents usable values given by Abbey[19]

	Granite G-2				
	UCR			USGS	
Element*	HCl	HF	Total	Range	Abbey
Si	0.060 ± 0.000	32.3 ± 0.050	32.4	32.2–32.3	32.3
Al	2.95 ± 0.017	5.35 ± 0.086	8.30	8.16–8.31	8.15
Fe	1.86 ± 0.008	0.020 ± 0.000	1.88	1.80–2.00	1.87
Mg	0.452 ± 0.005	<0.001	0.452	0.408–0.456	0.450
Ca	0.422 ± 0.005	1.00 ± 0.022	1.42	1.29–1.43	1.40
Na	0.512 ± 0.005	2.58 ± 0.214	3.09	2.82–3.07	3.01
K	2.49 ± 0.008	1.12 ± 0.037	3.61	3.69–3.82	3.70
Ti	0.260 ± 0.000	0.010 ± 0.000	0.270	0.282–0.294	0.288
B	4.75 ± 1.09	2.24 ± 0.329	6.99	—‡	—‡
Ba	1263 ± 5.00	683.0 ± 10.61	1946	1400–2100	1900
Be	<0.25	2.21 ± 0.194	2.21	2–3	2.4
Cd	<2.00	<2.00	<2.00	—‡	0.0397?§
Co	5.81 ± 0.539	<2.50	5.81	2–<10	5
Cr¶	4.83 ± 1.56	<1.00	4.83	7–12	8
Cu	11.0 ± 1.05	<5.00	11.0	9–14	10
Li	28.0 ± 0.311	<2.50	28.0	30–75	35
Mn	242.0 ± 1.29	2.65 ± 0.186	245	309–620	232
Mo	<4.00	<4.00	<4.00	<2–<10	—‡
Ni	<5.00	<5.00	<5.00	2–<7	3.5
P	483.0 ± 8.62	<2.50	483.0	567.0–699.0	568
Pb	—	—‖	—‖	20–50	30
Sc	3.32 ± 0.460	<0.500	3.32	<2–<7	3.5
Sr	118.0 ± 0.816	340.0 ± 28.4	458.0	340–400	480
V	31.4 ± 2.47	<5.00	31.4	30–50	36
Zn	77.1 ± 0.45	6.62 ± 0.657	83.7	—‡	84

* Values for Si. Al. Fe. Mg. Ca. Na. K and Ti given in %; values for the other elements given in mg kg^{-1}.
† Not determined.
‡ Usable values not reported.
§ ? implies a relatively greater degree of uncertainty.
¶ Incomplete dissolution.
‖ Values not reported because of the high coefficient of variation as a result of the low concentration near the detection limit.

measure elements within a linear concentration response range. Each fraction should therefore be analysed separately.

The HCl and HF sample solutions prepared in step 7 are 1 + 99 m/V dilutions. These solutions must be diluted further depending on the sample composition. For routine samples, we suggest a 1 + 4 dilution of each acid fraction from step 7 except when determining silica which is best analysed in a 1 + 499 dilution of the HF fraction. Samples such as peridotite and dunite which are high in Mg require a separate 1 + 99 dilution. The diluted HCl fractions are ready for analysis by ICP-OES using pneumatic nebulisation and/or hydride generation.

The sequence of using an oxidising agent first to destroy any organic matter followed by a final treatment with HCl has the added advantage that hydride-forming elements are kept in their reduced state and hence can be analysed by hydride generation in contrast to the more conventional final treatment with a strong oxidising agent such as $HClO_4$.

It should be noted that 6 M HCl suppresses the intensity of the signals from most elements by 15–20% compared with a <5% HCl matrix. The standard solutions used to calibrate the ICP-OES system were therfore prepared in the same HCl matrix and approximate major salt matrix as the samples. The zero concentration calibration standard was prepared by diluting distilled, constant-boiling HCl with resin-purified distilled water to the sample acid concentration. The high-concentration calibration standard was prepared to contain the same concentration of HCl plus 200 mg l^{-1} of Ca, 10 mg l^{-1} each of Mg and P. 100 mg l^{-1} each of Na and K and 1–8 mg l^{-1} each of the trace elements depending on the sensitivity of the element. Mixed calibration standards were prepared fresh for each sample set. If the indicated sample concentration values for an element exceeded the known

linear response for that element, then the sample was diluted and re-run until the concentrations in two two-fold dilutions agreed to within 3%. A reagent blank was processed with each set of samples to correct for contamination. The computer software corrected for spectral interferences by subtracting the interference signals from those of the analytes.

The following steps are suggested for hydride determination. Pipette a 30-ml aliquot of the 1 + 99 m/V solution from step 7 into a 40–50-ml glass test-tube. Place the tube in a boiling water-bath for 45 min to ensure reduction of the hydride-forming elements and analyse the sample by continuous hydride generation using ICP-OES.[18]

Results and Discussion

Analytical data for six USGS standard silicate rock samples are presented in Tables 2–7. The columns headed "HCl," "HF" and "Total" show the results obtained for the two acid fractions. The column headed "Range" indicates the range of measured values reported by Flanagan[17] using the complete, conventional rapid rock and spectrochemical analyses recommended by the USGS.

As noted by Shapiro and Brannock,[20] for the rapid analysis of silicate rocks by the USGS laboratories, Si and Al are determined spectrophotometrically using aliquots of a solution prepared by fusing the samples with NaOH: a Molybdenum Blue method is used for SiO_2, whereas Alizarin Red S is used for the determination of Al_2O_3. A second portion of the sample is digested with HF - H_2SO_4 - HNO_3 in FEP beakers and the solution is used for the spectrophotometric determination of total Fe with 1,10-phenanthroline, TiO_2 with Tiron. P_2O_5 with molybdovanadophosphoric acid. MnO as

Table 6. Concentration of mineral elements in USGS standard rock sample AGV-1. The UCR columns represent values obtained using H_2O_2 - HCl - HF dissolution and analysis by ICP-OES. The USGS column represents the range of values reported by Flanagan.[17] The Abbey column represents usable values given by Abbey[19]

Andesite AGV-1

Element*					UCR			USGS	
					HCl	HF	Total	Range	Abbey
Si	..	..	..	..	0.045 ± 0.006	27.7 ± 0.129	27.7	27.5–27.6	27.8
Al	..	..	..	..	5.05 ± 0.025	3.87 ± 0.008	8.92	9.05–9.21	9.10
Fe	..	..	..	..	4.67 ± 0.037	0.130 ± 0.000	4.80	4.52–4.90	4.77
Mg	..	..	..	..	0.908 ± 0.005	0.010 ± 0.000	0.918	0.840–0.960	0.912
Ca	..	..	..	..	3.30 ± 0.137	0.325 ± 0.006	3.63	3.36–3.49	3.53
Na	..	..	..	..	1.36 ± 0.008	1.35 ± 0.006	2.71	3.12–3.15	3.21
K	..	..	..	..	0.627 ± 0.005	1.76 ± 0.014	2.39	2.32–2.32	2.42
Ti	..	..	..	..	0.490 ± 0.000	0.070 ± 0.000	0.560	0.599–0.659	0.635
B	..	..	..	..	<2.50	6.56 ± 1.42	6.56	—†	6?‡
Ba	..	..	..	..	396.0 ± 3.16	496.0 ± 2.06	892.0	1200–1800	1200
Be	..	..	..	..	<0.25	1.10 ± 0.102	1.11	<2–<4	2?
Cd	..	..	..	..	<2.00	<2.00	<2.00	—†	—§
Co	..	..	..	..	10.5 ± 1.13	0.698 ± 1.12	11.2	10–18	16
Cr¶	..	..	..	..	—†	—†	—†	—†	—†
Cu	..	..	..	..	61.4 ± 1.58	<5.00	61.4	55–100	59
Li	..	..	..	..	<2.50	<2.50	<2.50	9–20	12
Mn	..	..	..	..	586.0 ± 4.35	6.00 ± 0.329	592.0	774.0–852.0	774
Mo	..	..	..	..	<4.00	<4.00	<4.00	4–<10	3?‡
Ni	..	..	..	..	13.1 ± 0.450	1.46 ± 0.550	14.5	7–18	15
P	..	..	..	..	1605.0 ± 19.2	<2.50	1605	2139–2314	2227
Pb	..	..	..	..	—‖	—‖	—‖	20–50	33
Sc	..	..	..	..	7.79 ± 0.079	<0.500	7.79	9–22	12.5
Sr	..	..	..	..	360.0 ± 3.16	138.0 ± 0.577	498.0	610–1000	660
V	..	..	..	..	99.9 ± 4.66	<5.00	99.9	80–150	125
Zn	..	..	..	..	49.0 ± 0.316	5.68 ± 0.250	54.7	—†	86

* Values for Si, Al, Fe, Mg, Ca, Na, K and Ti given in %; values for the other elements given in mg kg^{-1}.

† Not determined.

‡ ? implies a relatively greater degree of uncertainty.

§ Usable values not reported.

¶ Incomplete dissolution.

‖ Value not reported because of the high coefficient of variation as a result of the low concentration near the detection limit.

Table 7. Concentration of mineral elements in USGS standard rock sample BCR-1. The UCR columns represent values obtained using H_2O_2 - HCl - HF dissolution and analysis by ICP-OES. The USGS column represents the range of values reported by Flanagan.[17] The Abbey column represents usable values given by Abbey[19]

Basalt BCR-1

Element*					UCR			USGS	
					HCl	HF	Total	Range	Abbey
Si	..	..	..	..	0.080 ± 0.005	25.2 ± 0.082	25.28	25.2–25.3	25.4
Al	..	..	..	..	4.21 ± 0.180	2.96 ± 0.013	7.17	7.22–7.41	7.26
Fe	..	..	..	..	8.28 ± 0.010	1.14 ± 0.006	9.12	9.06–9.52	9.41
Mg	..	..	..	..	1.52 ± 0.059	0.420 ± 0.000	1.94	2.08–2.16	2.09
Ca	..	..	..	..	3.93 ± 0.024	1.08 ± 0.006	5.01	4.86–4.94	4.98
Na	..	..	..	..	1.19 ± 0.053	1.21 ± 0.005	2.40	2.30–2.46	2.46
K	..	..	..	..	0.387 ± 0.005	0.945 ± 0.006	1.33	1.33–1.41	1.41
Ti	..	..	..	..	1.27 ± 0.054	0.100 ± 0.000	1.37	1.32–1.35	1.35
B	..	..	..	..	<2.50	<2.50	<2.50	—†	4
Ba	..	..	..	..	157.0 ± 6.95	565.0 ± 2.39	722	400–900	680
Be	..	..	..	..	<0.25	0.281 ± 0.025	0.281	<2–<4	1.6?‡
Cd	..	..	..	..	<2.00	<2.00	<2.00	—†	0.09?‡
Co	..	..	..	..	<2.50	4.63 ± 0.281	4.63	26–40	36
Cr§	..	..	..	..	24.4 ± 3.12	<1.00	24.4	9–27	15
Cu	..	..	..	..	<5.00	<5.00	<5.00	19–35	16
Li	..	..	..	..	16.5 ± 1.25	<2.50	16.5	14–27	14
Mn	..	..	..	..	1065 ± 43.6	<2.50	1065	1471–1471	1394
Mo	..	..	..	..	<4.00	<4.00	<4.00	6–<10	1.5?‡
Ni	..	..	..	..	0.91 ± 2.77	1.87 ± 0.457	12.8	6–29	10
P	..	..	..	..	1322 ± 60.2	<2.50	1322	1528–2052	1572
Pb	..	..	..	..	—¶	—¶	—¶	32–50	14
Sc	..	..	..	..	23.2 ± 2.33	6.07 ± 0.412	29.3	<20–<20	33
Sr	..	..	..	..	207.0 ± 8.85	104.0 ± 0.500	311.0	300–400	330
V	..	..	..	..	379.0 ± 20.2	30.3 ± 2.84	409	170–490	420
Zn	..	..	..	..	58.8 ± 2.47	9.42 ± 0.403	68.2	—†	125

* Values for Si, Al, Fe, Mg, Ca, Na, K and Ti given in %; values for the other elements given in mg kg^{-1}.

† Not determined.

‡ ? implies a relatively greater degree of uncertainty.

§ Incomplete dissolution.

¶ Vaues not reported because of the high coefficient of variation as a result of the low concentration near the detection limit.

Table 10. Analysis of a soil, a sediment and a rock sample for Se and As to assess the accuracy of the H_2O_2 - HCl - HF dissolution method followed by analysis using ICP-OES with hydride generation. All values given in mg kg^{-1} unless indicated otherwise

	Se				Recovery/	As				Recovery/
Sample	Blank	Added	Expected	Measured	%	Blank	Added	Expected	Measured	%
Soil 266	0.471	4.00	4.47	5.01 ± 0.02	112	9.90	3.00	12.9	13.0 ± 0.435	101
	0.471	—*	—*	—*	—*	9.90	12.0	21.9	22.1 ± 0.451	101
Sediment 308	21.2	20.0	41.2	40.7 ± 0.30	98.8	3.85	3.00	6.85	6.95 ± 0.180	101
Rock 331	0.337	0.400	0.737	0.699 ± 0.051	94.8	4.58	0.400	4.98	5.11 ± 135	103

* Selenium was not added.

element in a sample and S_D is the standard deviation referred to D values of an element for n samples).

Table 8 presents the correlation coefficients and calculated t-values for measurements of Y_1, and Y_2. It should be noted that the test is performed independently of sample type. The high positive correlation coefficients indicate that a significant linear relationship exists between the data for the elements measured by the proposed dissolution method and those reported by Abbey.[19] The t-values are indicative of insignificant differences between the measured and reported data. It is almost impossible to expect a better agreement when the values obtained by ICP-OES are compared with those obtained from the spectrophotometric analysis using NaOH fusion techniques and/or with the values obtained from spectrochemical analysis of the solid inorganic forms using d.c. arc techniques.

Samples of colemanite ($Ca_2B_6O_{11}.5H_2O$) were digested and analysed by the proposed method. The measured value for B was 15.6 ± 0.01% compared with a calculated value of 17.5%. while the measured value for Ca was 19.7 ± 0.13% compared with a calculated value of 19.5%. Dissolution and analysis of samples of pure quartz (SiO_2) gave a value of 46.4 ± 0.1% for Si or an SiO_2 equivalent of 99.4%.

Table 9 presents data for the analysis of US Bureau of Reclamation standard reference samples. The column headed "USGS" shows the accepted values for Se based on ten replicate analyses by the USGS Laboratory Geological Division. The column headed "UCR (ICP-OES)" shows the results of the analysis of the sediment samples digested using the proposed method in our Trace Element Laboratory at the University of California, Riverside (UCR). Table 10 presents data for the digestion and analysis of a soil, a sediment and a rock sample with and without added Se and As. Both tables indicate good recovery and measurement of Se and As.

Separate analyses of the HCl and HF digests indicated that less than 2% of the Si was released by HCl and that dissolution was actually completed by treatment with HF. Boron in USGS samples was released and measured in the HF fractions only. whereas in colemanite it was completely dissolved by the HCl treatment. Addition of HF to this solution resulted in the precipitation of CaF_2.

Based on the above observations and a comparison of data. we recommend the two-step H_2O_2 - HCl and HF dissolution method followed by separate elemental analysis of each fraction of soil and geological material. However, for some applications, analysis of the HCl fractions may be sufficient.

To correct for problems caused by volatilisation of SiO_2 and B from glass components of the nebuliser assembly by dilute HF solutions. these components were reconstructed from poly(vinyl chloride) plastic pipes and used in the assembly for all the analyses. No dissolution of the glass torch by the dilute HF sample aerosol was observed.

Conclusion

Oxidation of organic matter breaks the structural units of soils and results in a more dispersed system. Hydrochloric acid then dissolves the salts and disperses the system further. Separation of dissolved materials from residues followed by repeated

treatment with acids at low temperatures in capped containers with agitation provides an optimum solid - liquid interface for a complete dissolution process with minimum losses of volatile constituents.

The time per sample treatment can be conveniently minimised by processing a large number of samples (50–100) simultaneously. Most steps in the procedure can be left unattended which reduces further the actual time spent in sample treatment. The procedure is easily followed in most chemical laboratories including those not equipped with a costly $HClO_4$ fume hood. The concentrations of elements found in six USGS standard rock samples compare favourably with values reported by other laboratories.

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APPENDIX E

ANALYTICAL PROGRAM FOR ICAP-OES

ANALYTICAL AND QUALITY ASSURANCE PROGRAM FOR

INDUCTIVELY COUPLED ARGON PLASMA

OPTICAL EMISSION SPECTROSCOPY (ICAP-OES) LABORATORY

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March, 1989

Emission spectroscopy instrumentation within the Department of Soil and Environmental Sciences at the University of California, Riverside has been applied to trace element studies of the soil-plant-water system since about 1930. Technological advances in instrument design, in quality of optical components, solid state electronics, computer controls and means of activating the sample have contributed to the development of present-day rapid, simultaneous multielement analytical instrumentation.

Procedures followed from time of sample receipt through sample identification, handling, storage, analyses and data processing are outlined in the following pages.

Sample types consist mainly of waters, plants and soils although others including biological, geological and a variety of environmental materials can also be analyzed after appropriate dissolution treatment.

SAMPLE COLLECTION AND IDENTIFICATION

Containers for sample collection are preferably made from polyethylene with tight-fitting screw-cap closures. A laboratory number is recorded on the container with a water-insoluble marker. Numbers are also recorded in a laboratory record book. The following additional information is recorded opposite the laboratory number:

1. Names and signatures of collectors

2. Date and time of collection

3. Place and address or description from where sample was taken

4. Signatures of persons involved in the chain of possession, with dates from the time of sample collection to analyses

5. Sample type:

   a) Water samples are identified as irrigation, drainage, well, surface, stream, rain, etc.

   b) Soil samples are identified as surface, profile, depth, etc.

   c) Plant samples are identified as type of plant, part, etc.

   d) Similar detailed information is entered for other types of samples in the sample record book.

SAMPLE PREPARATION AND STORAGE

Electrical conductivity and pH measurements are made on all water samples and soil water extracts before storage in a cold room (10°C). This information is entered in the laboratory sample record book and is referred to later for preparing dilutions of sample aliquots.

Soil samples are air-dried and homogenized with an agate mortar and pestle, sieved and then stored in covered polyethylene containers.

Plant samples are washed in tap water with a soft brush and a mild detergent, rinsed briefly in distilled water, dried with a clean cloth towel, and oven-dried in a forced draft at 60°C. Dried samples are

crushed by hand to avoid metal contamination from mechanical grinders, and then stored.

Dried soil and plant samples are stored in a secured laboratory space where they are free from contamination, loss or damage.

Samples to be analyzed for Se and Hg which are subject to loss by microbial or chemical volatilization or precipitation or adsorption by the container are cooled to 10°C at the time of collection and analyzed within five days.

SAMPLE PREPARATION FOR ANALYSES

Soil water extracts, usually 1:1 m/v, are prepared by adding a measured volume of deionized distilled water (DIDW) to the appropriate weight of soil and removing the soil water by suction filtration in an all-plastic system after a 24-hour equilibration period. Solution contact with rubber stoppers or tubing is avoided to prevent zinc contamination. Soil extracts are stored in a cold room (10°C). Appropriate dilutions (EC < 3 dS m^{-1}) of samples with a high salt content are made before direct analysis by pneumatic nebulization with ICAP-OES to avoid pronounced matrix and viscosity effects in the nebulizer.

Water samples high in salt content are also diluted to an electrical conductivity value less than 3 dS m^{-1} for direct analysis by ICAP-OES.

Since seawater, some soil water extracts and agricultural evaporation pond waters in arid regions are sufficiently saline to cause matrix

problems during analyses by ICAP-OES, it becomes necessary to pretreat these waters to separate and concentrate many of the trace elements. Separation of numerous trace metals from high salt waters for analyses by ICAP-OES is accomplished using a chelation solvent extraction method developed in our laboratory. Tests with low concentration spiked additions of Fe, Mn, Cu, Zn, Cd, Pb, Ag, V, Mo, Ni, Co, Cr^{+3}, Cr^{+6}, Tl, Ga, Se^{+4}, and U show 100% $\pm$ 5% recovery from synthetic saline solutions.

Plant and biological type samples are solubilized by wet oxidation at 70°C using concentrated HNO_3 and/or H_2O_2 in 50 ml screw-cap teflon centrifuge tubes.

Soils, sediments and geological type samples are dissolved by treatment with H_2O_2-HCl-HF (see appendix).

ICAP-OES INSTRUMENTATION AND OPERATING CONDITIONS

The ICAP-OES instrument in current use in our laboratory is a Jarrell-Ash Atomcomp 800 Series spectrometer with computer-controlled background correction including spectral line overlap correction and other timing and standardization functions. Mass flow controllers are used to control argon gas flow to the nebulizer and torch. A continuous flow hydride generation accessory is used for simultaneous determination of Se, As, Sb, Bi, Ge and Te as their hydrides and Hg as cold vapor. Spectrum line photographic records can be made on a Wadsworth spectrometer. A single channel .5 M Ebert spectrometer operates simultaneously with the other spectrometers.

A peristaltic pump is used to control sample solution flow to the nebulizer to minimize physical interferences associated with changing viscosity and surface tension of sample solutions. Nebulizer tips are made from teflon and other plastic material to reduce salt buildup.

Table 1 lists the wavelengths and estimated detection limits for elements analyzed in our laboratory by ICAP-OES. Operating conditions are listed below.

Argon flow:

Collant, 14 L min^{-1}

Sample, .5 L min^{-1}

Plasma, 0 L min^{-1}

Argon pressure to nebulizer, 60 psi

Nebulizer type, crossflow

Integration time, 17 s on line, 17 s background

Incident power, 1.25 KW

Reflected power, <10 W

Observation height, 13 mm above coil

Sample aspiration rate, 1.5 ml min^{-1}

REAGENTS

Reagent-grade acids are purified by distillation with a teflon condenser to reduce impurities from contact with glass.

Distilled water is purified by passing through a mixed bed of cation and anion exchange resin (DIDW). All reagents, calibration standards and dilutions are made with DIDW.

Standard stock solutions are made from ultra-high purity grade chemicals or metals and stored in screw-cap polyethylene containers. One mg L^{-1} dilutions of each stock solution are checked for impurities by analyses with ICAP-OES.

STANDARDS AND BLANKS

Four solutions of mixed calibration standards are prepared weekly from 2000 mg L^{-1} stock solutions to assure compatibility and stability. These are made at 4 times the desired high point calibration concentration, and equal volumes combined daily before calibration of the instrument. Concentrations of trace elements in the high calibration standard vary from 0.1 to 8 mg L^{-1} depending on their sensitivity. Major element concentrations in the final high calibration standard in mg L^{-1} are Ca, 200; Mg, 10; Na, 100; K, 100; and P, 10. Concentrations (mg L^{-1}) in an instrument check standard are Ca, 100; Mg, 5 and Sr, .5.

The zero and high concentration standards and samples are prepared in approximately the same acid matrix (1% HCl + .1% HNO_3).

A reagent blank is carried through the complete procedure and contains all the reagents in the same volumes as used in processing samples.

ANALYSES AND QUALITY CONTROL

The instrument is initiated according to the manufacturers' instructions and allowed to stabilize for at least 30 minutes.

The micrometer setting is adjusted to peak the mercury light profile monitor response.

A 1 mg L^{-1} cobalt solution is nebulized and the response peaked by checking the vertical and horizontal adjustments of a concave mirror which focuses an image of the plasma on the entrance slit to the spectrometer.

A computer function is initiated to display raw intensities for each analyte channel and several typical sample runs processed with the zero calibration standard solution. This confirms that all channels are functioning and that the zero standard is free from contamination.

The high point calibration standard solutions are prepared and the instrument calibrated by running a zero point calibration standard and a high point calibration standard for each of two mixed calibration standards.

The raw intensity values for both zero and high point calibrations are displayed and the values printed. These values are visibly checked and compared to previous days' runs to identify that all channels are functioning, are properly profiled and/or that all analyte elements are in solution and responding at the expected intensity levels. These data are recorded with each set of samples and are an invaluable source to identify contamination and/or other quality control problems which might otherwise go undetected.

An instrument check standard, a zero calibration blank, and duplicate samples are run at a frequency of 10% to verify alignment and nebulizer stability. Calibration standards are run at the beginning and after each set of samples. If results do not agree within ±5%, the instrument is recalibrated and the samples rerun.

If indicated sample concentration values for any element exceed the known linear response for an element, then the sample is diluted with DIDW and rerun until the concentrations in two 2-fold dilutions agree within ±5%. If an unusually high or unexpected concentration of an element is indicated in a sample, a photographic record is made and examined with a densitometer which enables qualitative confirmation by identification of several spectrum lines of the element.

A quality control sample (sample obtained from an outside source having a known concentration value) is analyzed on a weekly basis.

Instrument printout data sheets are filed in the laboratory. A floppy disk record of data is transferred to an IBM PC-XT for statistical analyses and permanent storage.

Our laboratory participates in the University of California, Davis and the U.S. Geological Survey's analytical evaluation programs.

Table I. ICAP-OES wavelengths and estimated** instrumental detection
         limits.

Element	Wavelength (nm)	Estimated detection limit (mg/L)
Aluminum	308.21	0.03
Arsenic	193.69	0.001*
Antimony	206.83	0.001*
Barium	493.40	0.002
Beryllium	234.86	0.0005
Boron	249.67 II	0.005
Bismuth	223.06 II	0.001*
Cadmium	228.80 II	0.004
Calcium	317.80	0.050
Chromium	267.71	0.002
Cobalt	228.61	0.005
Copper	324.75	0.010
Gold	242.80	0.005
Gallium	417.21	0.020
Germanium	199.82	0.001*
Iron	259.94	0.005
Lanthanum	379.48	0.010
Lead	220.35	0.020
Lithium	670.70	0.005
Magnesium	279.55	0.020
Manganese	257.61	0.005
Mercury	253.65	0.001*
Molybdenum	202.03 II	0.008
Nickel	231.60	0.010
Potassium	766.40	1.0
Phosphorus	214.91	0.050
Selenium	196.02	0.001*
Scandium	341.38	0.001
Silicon	251.61	0.010
Silver	328.06	0.005
Sodium	588.90	0.20
Strontium	421.50	0.008
Tellurium	214.20 II	0.001*
Thallium	190.86 II	0.100
Thorium	401.91	0.030
Tin	284.00	0.100
Titanium	334.90	0.010
Tungsten	207.91	0.020
Uranium	385.96	0.20
Vanadium	292.40	0.010
Yttrium	371.00	0.005
Zinc	206.20 II	0.005
Zirconium	339.2	0.005

II second order lines
*   continuous hydride system with ICAP
** detection limits vary with sample matrix; detection limit is defined
    as the concentration equivalent to a signal due to the analyte, which
    is equal to three times the standard deviation of a series of 10
    replicate measurements of a zero calibration blank.